SPONTANEOUS EMULSIFICATION: MECHANISMS, PHYSICOCHEMICAL
ASPECTS AND APPLICATIONS

By

JUAN CARLOS LOPEZ-MONTILLA

I dedicate this effort to the people I love the most: my beloved mother Bertha Eduviges Montilla de López, to my daughter Johanna Isabel López Durán, my girlfriend Kivanç Turkoglu and my friend Carmen de Los Rios, and to the memory of my father Rafael Alejandro López and of my grand grandmother Francisca López.

ACKNOWLEDGMENTS

I have not words to thank Dr. Dinesh O. Shah for what he has done for me. The written and spoken languages are not appropriate languages to describe the feeling of gratitud that I have for him. I can just say that I love him. I thank God for allowing me to meet Dr. Shah.

To Kivanç Turkoglu, the love, the unreachable dream, the woman who tooke care of me during the last one and a half year of my studies. I will never forget her great dedication to me and the happiness she gave to me.

There is a great woman named Carmen de Los Rios, without whose help I would not have been able to come here. She is the friend every one dreams to have, and she is just amazing. I thank Carmen for ever.

I would also like to thank the following persons: Dr. Oscar Crisalle for giving me the unique opportunity for joining the University to pursue my Ph.D. studies; Dr. Jean Luis Salager, who has been a great support and inspiration since I met him; Dr. Conxita Solans, a brave woman, for her invaluable help in leading me to understand the phase behavior of surfactant-oil-water systems.

TABLE OF CONTENTS

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

SPONTANEOUS EMULSIFICATION: MECHANISMS,
PHYSICOCHEMICAL ASPECTS AND APPLICATIONS

By

Juan Carlos Lopez-Montilla

May 2003

Chair: Dr. Dinesh O. Shah
Major Department: Chemical Engineering

This dissertation comprises my research in spontaneous emulsification to produce

thermodynamically unstable nano-emulsions. First, a new method to quantitatively

determine the spontaneity of the emulsification process was designed. Second, with this

method on hand, different factors affecting the drop size distribution and the mechanism

of spontaneous emulsification were assessed (oil-chain-length, surfactant structure,

surfactant-concentration, pH, salinity, synergism of surfactant mixtures). Third, it was

shown that the presence (or formation and posterior destruction) of liquid crystal is an

essential requirement for the formation of nano-emulsion with low energy consumption.

Fourth, a correlation between spontaneous emulsification mechanism and drop size

distribution was established. Here, it was shown that instabilities induced to the

structures on self-assembled systems such that liquid crystal and bicontinuous

microemulsion lead to the formation of emulsions with nano-size drops (< 1 μm). On the

other hand, instabilities induced to interfaces of the hydrodynamic kind such as Raleigh-like instabilities or interfacial turbulence lead to emulsion with large-drops (40-100μm). Furthermore, instabilities via diffusion and stranding produce emulsion with medium drop size (1 to 20 μm). Fifth, it was shown that surfactant structure, surfactant concentration, and surfactant application protocol are the keys to spontaneously remove oil (soil) from polyester fabric. It was also shown that these factors control the main mechanisms (rollback and spontaneous emulsification) for spontaneous detergency of oil. Sixth, it was shown that the spontaneous emulsification and the molecular interaction at the interface and in bulk phases are key factors to consider for the removal of hazardous molecules (e.g., phenol) from water. Finally, it is important to stress the fact that nano-emulsions are very important systems in science as well as in technology and this research showed the mechanism and emulsification protocol to produce emulsions with different drop sizes including nano-size (nano-emulsion).

CHAPTER 1
STATE OF THE ART

1.1 Introduction

Emulsions are thermodynamically unstable material systems formed by at least two immiscible liquid phases, one of them dispersed in the other(s). When an emulsion separates into its bulk phases the free energy of the system decreases due to the decrease in interfacial area. Therefore, to generate these systems from liquid phases initially at equilibrium, energy must be supplied, generally by mechanical means, most of which is lost to viscous dissipation. Furthermore, if emulsion drop size must be small, a much greater amount of mechanical energy would be necessary [Miller, 1988], since the work required (W) to increase an interface is

$$W = \Delta A \cdot \gamma \qquad (1-1)$$

where ΔA is the increase in the total interfacial area and γ is the interfacial tension. This relationship suggests that the larger ΔA is (i.e., smaller droplet size for a fixed volume fraction of dispersed phase), the larger the amount of work needed to produce an emulsion.

Nevertheless, there are a variety of systems spontaneously formed by two immiscible liquid phases with the help of at least a third component (generally a surfactant), which are known to form thermodynamically stable "dispersions" as well [Shahidzadeh, 999]. In some of these systems (e.g., microemulsions) the characteristic size of the dispersed "domain" is much smaller than in an emulsion (< 100nm). These microemulsions are characterized by (a) an ultralow oil-water interfacial tension, which

1

greatly facilitates the formation of the large interfacial area, and (b) the sizes of the dispersed droplets that are much smaller than those of an emulsion, which increases the entropy of mixing and their stabilization [Shahidzadeh, 1999].

The existence of systems such as the microemulsion depicted above suggests that under certain conditions an emulsion can spontaneously be formed. If the bulk liquid phases are not initially at equilibrium, it is conceivable that certain dynamic processes such as diffusion, thermal fluctuations, or ultralow or transient negative interfacial tension could lead to emulsification when the phases are brought in contact without stirring [Miller, 1988], or significant mechanical work done. Furthermore, phase inversion induced by temperature changes could also lead to the spontaneous formation of an emulsion [Kunieda, 1996].

The first observation of a possible spontaneously formed emulsion was made in the 19th century. In 1878 Johannes Gad observed that a solution of lauric acid in oil spontaneously formed emulsions when placed on top of an aqueous alkali solution [Quincke, 1879]. After the discovery made by Gad, investigations have thrown some light on the phenomenon, but certain features of the mechanisms which may be involved are still very much matters for discussion [Groves, 1978].

Before going further, it is important to clarify two terms that are usually encountered in the literature related with this topic (a) spontaneous emulsification and (b) self-emulsification. True "spontaneous emulsification" occurs when (1) two immiscible liquids are placed in contact with each other and emulsify without the aid of any significant external thermal or mechanical energy source -- depending on the liquids involved, it may take from a few minutes to several days for completion--, or (2) when

the temperature of a system crossing through a so-called sponge phase, L_3, [Brand, 2002; Gomati, 2002; Hellweg, 2002] is changed to undergo the phase-inversion. On the other hand, in industrial practice, emulsification is often achieved with the aid of suitable surfactants and is loosely called "self-emulsification," even though the emulsification process is helped by providing mechanical energy of some form, such as slight shaking, mixing [Groves, 1978], or sonication.

Spontaneous emulsification is produced by different mechanisms which seem to be affected by the system composition, the physicochemical characteristics and the protocol of emulsification (i.e., the way in which the components are added and how the thermodynamic properties of the system are changed). Three main possible mechanisms have been proposed by previous researchers [Davies, 1957; Davies, 1961a; Davies, Davies, 1961b]. Two of them involved mechanical breakup of the interface due, in one case, to the intensity of interfacial turbulence and, in the other, to the existence of negative values of interfacial tension [Davies, 1957; Davies, 1961a]. The negative interfacial tension criterion is an oversimplification because factors other than tension (e.g., electrical forces in double layers) can significantly influence stability when tension is low (less than about 1 mN/m). Thus, this second mechanism is better described as mechanical instability of low-tension interfaces [Davies, 1961b]. The third mechanism was called "diffusion and stranding" by Davies and Rideal and is entirely different from the previous two because it involves a chemical instead of a mechanical instability. The basic idea in this case is that regions of local super-saturation are produced by the diffusion process and the emulsion droplets form due to phase transformation in these regions. Super-saturation near an interface may also promote its breakup by a distinct but

closely related chemical instability mechanism. This mechanism is best known as the main cause of dendrite formation during solidification [Davies, 1961a; Ruschak, 1972]. A theoretical treatment for both the negative interfacial tension and the diffusion and stranding mechanisms is available in the literature [Granek, 1993; Ruschak, 1972], although, the description is limited to over-simplified models.

With the continuous development of new and improved experimental techniques, more mechanisms of spontaneous emulsification have been proposed, such as (a) explosion of a bilayer structure as a consequence of the osmotic pressure gradient [Shahidzadeh, 1997], (b) transition in the sequence of the structure curvature due to temperature or concentration gradient [Forgiarini, 2000; Forgiarini, 2001; Kunieda, 1996], and (c) inversion of a micellar solution by swelling of the micelles due to osmotic pressure [Greiner, 1990].

Another main characteristic of the spontaneous emulsification process, besides its mechanisms, is the spontaneity of the emulsification. This, however, has been poorly defined, since it should account not only for the rate of the emulsification process, but also for the volume and the particle size distribution of the produced emulsion. The spontaneity of the emulsification process depends mainly on following variables: spreading pressure, interfacial tension, interfacial and bulk viscosity, and surfactant, co-surfactant, oil and aqueous phase composition (i.e., component's structure and their concentration), temperature, salinity, and mixing component protocol [Davies, 1961a]. The technique amply used industrially to measure the spontaneous emulsion formation is known as the Collaborative Pesticide Analytical Committee of Europe test (CPAC test), which evaluates qualitatively the ease of emulsification (see sections 1.6 and 3.2.1).

An improved understanding of the spontaneous emulsification process is also motivated by the fact that the emulsification process and the emulsion produced are of key importance for a large number of industrial applications such as self-emulsifying oils for pesticides, enhanced oil recovery, drug delivery systems, personal-care products and preparation of foodstuffs, among others.

Finally, for an easy search of the different systems in which spontaneous emulsification has been observed, the reader is suggested to review the Table A-1 that appears in the appendix. In this table, the author has compiled a number of systems that have been studied by various researchers in different areas of investigation and/or industrial application.

1.2 Mechanisms of Spontaneous Emulsification

The amount of energy necessary to generate a new interfacial area in a system formed by two immiscible liquids in order to produce an emulsion is very small [Walstra, 1983]. However, the actual energy required to generate the whole emulsion is at least 1000 times larger. For instance, assume the following conditions: (a) oil droplets with a radius r = 1 μm formed in water, (b) internal phase volume fraction $\Phi = 0.1$ and (c) interfacial tension $\gamma = 10$ mN/m; then the surface free energy amount needed or required to generate an emulsion is ~ 3 kJ/m^3, while the energy actually needed to produce the emulsion would be at least 3 MJ/m^3 (which can generally be obtained by means of very intense agitation). Except for the tiny fraction that is needed for the interfacial free energy, this energy is mainly lost by means of viscous dissipation of energy by the two liquids [Walstra, 1983].

Considering the above discussion, how is it possible that emulsions can form spontaneously without violating the second law of thermodynamics? Observations that

support this phenomenon were first made in the second half of the 19th century [Quincke, 1879; Quincke, 1888]. For instance, when two immiscible liquids which are not initially equilibrated are brought in contact, certain dynamic processes and phenomena may induce spontaneous emulsification without the aid of mechanical stirring [Miller, 1988]. Also, when the temperature of a homogeneous system like a microemulsion (which is already at equilibrium) is changed, the phase transition that is produced leads to a spontaneous emulsion formation [Kunieda, 1996]. Finally, if a water-in-oil (w/o) microemulsion (containing brine and oil) is in contact with water, osmotically driven water into the w/o microemulsion promotes the size increase of the microemulsion droplets, which eventually will come into contact and generate an emulsion [Greiner, 1990].

Based on these observations and on the fact that an emulsion can be produced by dispersion or condensation, several mechanisms for spontaneous emulsification have been proposed [Davies, 1961a]. In a review made in 1961, three mechanisms are presented (a) interfacial turbulence, where convective flow of materials are generated due to interfacial tension gradients caused by uneven concentration of surface active molecules at the interface; (b) transient negative interfacial tension, which cause the spontaneous expansion of the interfacial area [Miller, 1988], and (c) "diffusion and stranding, " where the emulsification occurs due to condensation of one liquid upon diffusive separation of the second liquid component.

The improvement and the appearance of new experimental techniques and the study of different systems have led to a few new mechanisms for spontaneous emulsification discussed later in this chapter.

1.2.1 Original Mechanisms

As indicated above, three principal mechanisms had been proposed to explain the spontaneous formation of emulsions up to 1961 (1) interfacial turbulence, (2) negative interfacial tension, and (3) diffusion and stranding. Even though these mechanisms have been the subject of controversy, they remain as important references for spontaneous emulsification studies [Davies, 1961b].

1.2.1.1 Interfacial turbulence

In many cases of spontaneous emulsification, if one places a drop of the lighter liquid on top of the heavier one, the interface starts to develop unsteady motions, which are described as "kicking". Very often fingers or streamers start out from one phase and penetrate slowly through the other one, shedding smaller droplets as they go. This suggests that there is some form of interfacial instability and was the basis for what has been proposed as the interfacial turbulence mechanism [Davies, 1961b].

In 1878 Gad [Quincke, 1879] had noticed that when solutions of lauric acid in oil are placed very gently on aqueous sodium hydroxide, an emulsion is formed in the water phase. Quincke [1879] explained the observations of this work, and later [Quincke, 1888], he suggested that the spontaneous emulsification is caused by localized interfacial tension gradient, due to the non-uniform distribution of the soap molecules formed along the interface [Quincke, 1888]. This would lead to violent spreading of the soap molecules on the interface which generates interfacial turbulence at these spots; threads of one liquid are thrown into the other liquid, where they disintegrate into droplets. Droplets traveling into the other phase may become stabilized by some mechanisms not necessarily related to the interfacial turbulence and form stable emulsion droplets [Groves, 1978; Quincke, 1879].

It has been found that generally the interfacial turbulence mechanism acts in combination with other mechanisms. For example, a good system to test for this mechanism is that of methyl or ethyl alcohol in toluene in contact with water. This system presents strong spontaneous emulsification and marked interfacial turbulence. The emulsification in these systems also have contributions from another mechanism (see section 1.2.1.2) since the interfacial turbulence can be completely suppressed by adding a little amount of detergent to the water, by dissolving salt in the water, or by spreading a protein film at the interface, while the spontaneous emulsion could still be produced [Davies, 1961a].

1.2.1.2 Diffusion and stranding

The main characteristic of the "diffusion and stranding" mechanism is that its occurrence is "independent" of the value of the interfacial tension, which may be relatively high. A good example for this mechanism occurs when a solution of ethyl alcohol and toluene is placed gently in contact with water. The alcohol, as it diffuses from the oil into the water, carries with it some oil (forming a three-component phase in the immediate vicinity of the interface). As the alcohol diffuses further into the water, the associated oil becomes thrown out of solution, and is "stranded" in the water in the form of fine emulsion drops. Simultaneously, drops of water may also appear on the oil side of the interface, since the alcohol in the oil may permit some water to dissolve. As the alcohol passes into the aqueous phase, the water becomes "stranded" in the oil. This mechanism is likely whenever the third component increases considerably the mutual solubility of the oil and the water. Thus, mixtures of an oil with sulfonated castor oil and sodium oleate (used as surfactant) brought in contact with water emulsify due to the sodium oleate molecules carry oil with it into the water [Davies, 1961a]. This

emulsification mechanism can be visualized in Figure 1-1 and the schematic diagrams shown in Figures 1-2 and 1-3.
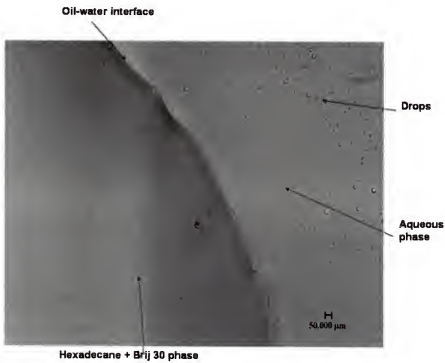
Figure 1-1.   Diffusion and stranding mechanism depicted by the behavior of a drop of hexadecane-$C_{12}E_6$ system after being put in contact with a drop of water at room temperature (this experiment was run on a microscope slide).

The rate of the emulsification process is diminished by reducing the interfacial turbulence with surfactants and/or salts dissolved in water, in systems where solutions of methanol or ethanol in toluene are placed gently in contact with water. Furthermore, for these systems, the equilibrium interfacial tension is always positive, of the order 10 mN/m, leaving the diffusion and stranding mechanism as the main one for its spontaneous emulsification. By pre-saturating the toluene-alcohol mixture with water, one does not observe spontaneous emulsification. This suggests that transfer of alcohol from oil into water and/or water into oil is an important required condition for

spontaneous emulsification using diffusion and stranding mechanism. The diffusing

alcohol leaves much water stranded in the oil, as well as the oil stranded in the water.
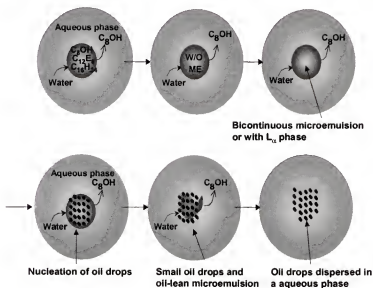
Figure 1-2. Schematic diagram showing the spontaneous emulsification process for a drop of n-hexadecane/n-octanol(C_8OH)/$C_{12}E_6$ contacting water [Rang, 1999].

1.2.1.3 Negative interfacial tension

The most straightforward illustration of the effect of a negative interfacial tension

on the expansion of the interfacial area is the spontaneous emulsification of mercury in

water. It was shown that if a negative potential is applied to a mercury drop in an

aqueous solution of a quaternary ammonium salt, the interfacial tension could be greatly

decreased [Davies, 1961a]. The electrocapillarity curve for this system, which is a

representation of the interfacial tension, is shown in Figure 1-4. The quaternary

ammonium ion is so resistant to decomposition at the surface of the mercury that a highly

compressed monolayer of these cations is held there, both by adsorption of the

hydrocarbon residues and by electrical attraction. At a potential of about –2.2 volts, the

extrapolation of the electrocapillarity curve suggests that the interfacial tension must

become negative. The negative interfacial tension at large applied negative potential results in disintegration of the surface of the mercury drop into a brown cloud of colloidal mercury in water, and at -8 volts the spontaneous emulsification is very striking [Davies, 1961a].
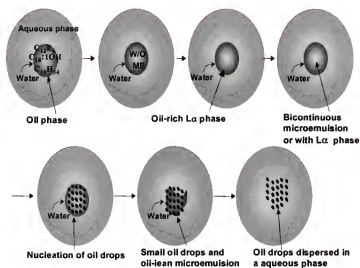
Figure 1-3.   Schematic diagram showing mechanism of spontaneous emulsification for a drop of oil containing suitable amounts of nonionic surfactant and alcohol [Nishimi, 2000].

It has also been suggested that certain water-oil-surfactant systems could emulsify under the negative interfacial tension mechanism as well. When, for example, toluene containing cetyl alcohol is placed on top of aqueous solutions of sodium dodecyl sulfate, spontaneous emulsification will take place when the concentration of alcohol or detergent exceeds a specific concentration limit [Davies, 1961a; McBain, 1937; Schulman, 1940]. The interfacial tensions of this system have been measured at the lower limits and it was found that they could be extrapolated to zero values [Davies, 1957]. Thus, it has been suggested that at the higher surfactant or co-surfactant concentrations, the interfacial tensions could transiently be very small or negative [Miller, 1977; Prince, 1967]. Under

these conditions the interfacial area would spontaneously increase by forming a number

of droplets which would be ejected into a new environment where the interfacial tension

could once again become positive and the droplets would be stabilized by surfactant film

[Groves, 1978]. A similar mechanism was proposed when a drop of toluene is brought in

contact with an aqueous solution of dodecylamine.
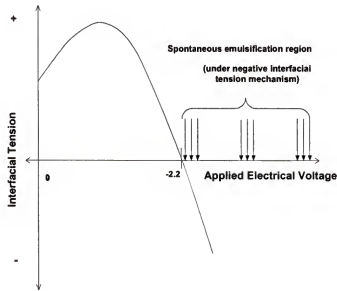
Figure 1-4. Interfacial tension of mercury in an aqueous solution of a quaternary
ammonium compound as a function of an applied electrical potential
[Davies, 1961a].

    A curious characteristic of the systems that could present transient negative

interfacial tension is that one would expect spontaneous emulsification, but the

phenomenon is not observed because of huge interfacial or bulk viscosity. In this case,

the surface area increases not by droplet formation but by folding. An example of this

situation is that of rapidly compressed film of protein at an oil-water interface [Davies,

1961a].

    Of the original three mechanisms proposed to explain spontaneous emulsification,

the negative interfacial tension mechanism is the one that has been criticized the most.

Several researchers have denied the existence of a negative interfacial tension [Prince, 1967]. Some of them argue that when, in at least one case, the extrapolated negative values obtained by Davies and Haydon [1957] were reexamined taking greater care, the values turned out to be very small (0.005 mN/m) but positive (referred as ultralow interfacial tension). Nevertheless, in the case of spontaneous emulsification, one is not concerned with the equilibrium but with the transient dynamic interfacial tension. Thus, even if the equilibrium interfacial tensions are positive, the possibility of momentary negative values of it existing along the interface cannot be ruled out [Groves, 1978].

A simple mechanism has been suggested for the lowering of interfacial tensions to very low values, 10^{-3} mN/m or lower [Chan, 1981; Matalon, 1950; Miller, 1977; Shah, 1980]. This study showed that systems with low interfacial tensions are often associated with the formation of weakly birefringent material at the oil-water interface. Therefore it was suggested that large micelles containing solubilized oil could separate out at or close to the interface. The effect of this would be to lower the net interfacial interaction energy per unit area and reduce the interfacial tension [Groves, 1978].

Finally, a good example to explain a transient negative interfacial tension is a system made from water and oil, to which potassium oleate and a medium chain alcohol are added as surfactant and co-surfactant, respectively (see Figure 1-5). The initial water-oil interfacial tension (γ_0) is a positive value Figure 1-5a. When potassium oleate is added to this system, the resulting interfacial tension (γ_f) will be lower than the one for the original system as a consequence of the potassium oleate adsorbed at the interface, but it is still positive (see Figure 1-5b). The spreading pressure (π), which is the driving force for the expansion of the interface, is defined as $\pi = \gamma_0 - \gamma_f$. Now, if one adds a co-

surfactant (e.g., a medium chain alcohol), the transient spreading pressure could reach

values greater than γ_0 in certain regions at the interface as a consequence of the increase

in the concentration of surface-active molecules (both oleate plus medium chain alcohol)

at the interface, as shown in Figure 1-5c. Since the original interface has some rigid

boundaries (i.e., the glass wall boundaries) the interface will tend to fold as shown in

Figure 1-5d. This process leads to a spontaneous increase in the interfacial area by

folding of the interface, with the consequent formation of an emulsion.
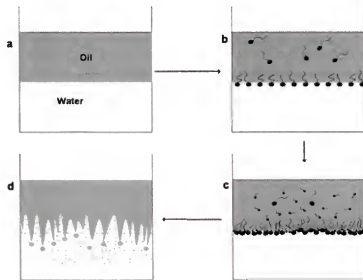
Figure 1-5. Graphic representation of the appearance of transient negative interfacial
tension for a water/oil/potassium-oleate/medium-chain alcohol system. (a)
System with pure water and oil, (b) addition of potassium oleate, (c)
addition of medium chain alcohol, and (d) deformation of the interface.

1.2.2 Recently Proposed Mechanisms

With the continuous development of new and improved experimental techniques,

more mechanisms of spontaneous emulsification have been proposed after the three

previous ones were presented in the work of Davies and Rideal [1961b]. These new

mechanisms include studies related with phase transition due to temperature changes,

osmotic pressure gradient effects, formation of myelinic figures (see Figure 1-6) at the water-oil interface, etc.
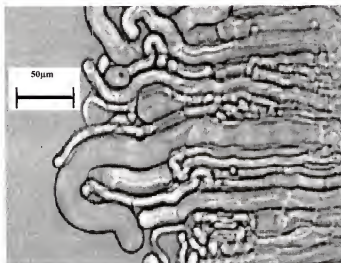
Figure 1-6.   Example of myelinic figures growth and interface [Buchannan, 2000].

It is worth noting that even though these mechanisms have not been given specific names by the researchers who proposed them, they are presented here with appropriate subtitles.

1.2.2.1 Explosion of vesicles by osmotic gradient

Shahidzadeh et al. [1997] proposed a mechanism related to the surfactant phase behavior and to the molecular architecture. They showed that salty aqueous solutions of the anionic surfactant sodium bis-2-ethylhexylsulfosuccinate (AOT) form vesicular rather than micellar structures, because the head and tail group of AOT are nearly balanced. When they brought these phases gently into contact with oil, they observed a flow of the surfactant aggregates towards the oil phase. The incorporation of the oil into the surfactant bilayers leads to the formation of oil films within the bilayers that are unstable. The vesicles are consequently destabilized and "explode, " thereby dispersing the oil into the aqueous phase.

According to Shahidzadeh et al. [1997] the alkanes incorporate spontaneously into the AOT bilayers, and that the critical micellar concentration in the presence of alkanes, CMCn, is smaller than in the absence of alkanes, CMCo. The shorter the alkane chain is the better solvent for the hydrophobic tails of the surfactant it is and, therefore, the smaller CMCn of the AOT in it. As the spontaneous emulsification proceeds through the incorporation of oil in the bilayers, it should be more efficient for the shorter alkanes to dissolve into bilayers than longer alkanes, since CMCn is much smaller than the CMCo (i.e., $CMC_{hexadecane} > CMC_{hexane}$).

A second important point is that, once a sufficient amount of oil is incorporated into the bilayers, the bilayers are unstable and lead to the destruction of the vesicles. In a different experiment under the same experimental conditions, Shahidzadeh et al. [1997] observed that AOT films swollen with oil and in contact with the aqueous phase have a lifetime that is typically less than 1 second. The external bilayers of these structures incorporate the alkane and do not allow for the penetration of oil in the internal part. This results in an osmotic pressure difference between the inside and the outside of a bilayer or vesicle and consequently induces the observed inflation of the vesicles and tethers far from the alkane reservoir [Shahidzadeh, 1997].

Shahidzadeh et al. [1997] also explain that at the earliest stages of the emulsification process, the observed hydrodynamic flow is Marangoni-driven (i.e., due to the interfacial tension gradients). However, once vesicles coat the entire oil-brine interface, another mechanism must take over, because the flow persists for long times (several tens of minutes). During the spontaneous emulsification, concentration gradients of the surfactant are formed. These are equivalent to chemical potential gradients which

could in principle act as a force on the vesicles. (An industrial application for this mechanism, the Mayonnaise production, is presented in section 1.5.5.)

1.2.2.2 Inversion of a highly viscous w/o microemulsion by osmotic gradient

Greiner and Evans [1990] proposed a mechanism of spontaneous emulsification which involves inversion of a highly viscous w/o microemulsion, based on their work with the microemulsion formed from the methyl ester of partially hydrogenated rosin containing 5 % w/w of the potassium salt of partially hydrogenated rosin acid and small amounts of water, by a quiescent adjacent water phase. In this system, inversion of w/o microemulsions leads to the formation of stable, rather homogeneous oil-in-water (o/w) emulsions containing oil droplets as small as 150 nm.

This mechanism involves osmotically driven swelling of inverted micelles in w/o microemulsion which remain fixed in a small volume element because of its high viscosity. The osmotic pressure inside the inverted micelles contained in the microemulsion phase is considerably lower than that of the contacted deionized water phase because of the high concentration of counterions. Because of the high viscosity of the medium and packing constraint, the micelles remain fixed as they swell with the aqueous phase, and eventually they invert. The small, uniform size of the resulting emulsion droplets is thus set by the constraints of the initial microemulsion structure. Immediately after the inversion process, the emulsion droplets, which are stabilized by an anionic surfactant, behave as a concentrated colloidal dispersion. The electrostatic repulsion between droplets drives them apart, and they move into the adjacent water phase.

Nevertheless, spontaneous emulsification leading to small, nearly uniform oil droplets does not occur when the initial bulk water content exceeds 10 % w/w. Above

this concentration, water from the adjacent aqueous phase simply fluxes into the oil phase and results in the formation of a coarse heterogeneous emulsion. Heating the microemulsion and water to 60°C before bring it in contact with water also leads to a coarse emulsion.

1.2.2.3 Sequential changes in structures (by temperature gradient)

In early work presented by Matalon [1950] the temperature dependence of spontaneous emulsification is hinted. However, Kunieda et al. [1996] and Pons et al. [1994] studied in detail the spontaneous formation of w/o gel emulsions from oil-swollen micellar solution (o/w microemulsions) with a rapid increase in temperature in a water/$C_{12}E_4$/oil system. Nevertheless, it is not completely evident that this is a spontaneous process, since some energy must be supplied to the system to increase the temperature in order to obtain the emulsion, even though there is not any mechanical energy.

Nevertheless, highly concentrated o/w emulsions are spontaneously formed by a rapid decrease in temperature in the 0.1 M NaCl aqueous solution/hexaethylene-glycol/dodecyl-ether/monolaurin/n-decane system, according to Kunieda, Solans and coworkers [Ozawa, 1997]. In this case, the spontaneous curvature of the surfactant molecular layer changes from concave to convex toward water with decreasing temperature. This is due to the fact that surfactant self-organizing structures change from a w/o microemulsion to a highly concentrated emulsion via lamellar liquid crystal and reverse bicontinuous (reverse L_3) phases.

Polyoxyethylene-type nonionic surfactants change from hydrophilic to lipophilic with an increase in temperature. At lower temperature, these surfactants dissolve in water as micelles, and oil is solubilized in them. With increasing temperature, the

solubilization of oil in the micelles is increased and, eventually, oil-swollen micelles are separated from water as a surfactant phase or microemulsion. This transition temperature is called the hydrophilic-lipophilic-balance (HLB) temperature. Above the HLB temperature, the curvature of the surfactant film reverses. The oil-continuous micellar solution and the excess water phase are formed. Hence, the spontaneous curvature of the surfactant molecular layer changes from convex to concave toward water with increasing temperature.

Finally, it is worthwhile to remark that Förster, et al. [1995] studied the influence of temperature changes on the drop size of an emulsion. They presented different emulsification routes as a function of the temperature. All components were mixed at room temperature and emulsified at 80°C and a liquid crystal phase occurred. They found that after cooling, a fine-disperse oil phase is obtained with a mono-modal droplet distribution of approximately 100 nm [Förster, 1995]. A detailed description of the correlation of this mechanism with phase diagrams is presented in the section 1.3.2.

1.2.2.4 Sequential changes in structures (by concentration gradient)

Forgiarini et al. [2000, 2001] studied the formation of nano-emulsions in the water/Brij30/decane systems at 25°C by three low-energy emulsification protocols (see Figure 1-7) (A) stepwise addition of oil to a water-surfactant mixture, (B) stepwise addition of water to a solution of the surfactant in oil, and (C) mixing all the components at the final composition. The emulsion composition had a 5.0 % w/w surfactant and an oil weight fraction, S, ranging between 0.2 and 0.8. They obtained nano-emulsions with average droplet size of 50 nm and high kinetic stability only with protocol B, at oil weight fractions, S, lower than 0.3. Independent of S, emulsions obtained by protocol B have lower polydispersity than those obtained by protocols A and C. Furthermore,

Forgiarini et al. [2001] showed that equilibrium properties cannot fully explain nano-emulsion formation, since low values of equilibrium interfacial tensions and phase equilibrium involving a lamellar liquid crystal phase are probably required but not sufficient to obtain nano-emulsions in this system. Probably, the spontaneous emulsification mechanism for the protocol B followed by Forgiarini et al. [2001] is similar to the mechanism proposed by Kunieda, Solans and coworkers (see section 1.3.2), where the spontaneous emulsification is promoted by decreasing the temperature. A detailed description of the correlation of this mechanism with the phase diagrams is presented in the section 1.3.3.

Förster, [1995] also studied the effect of surfactant concentration on the drop size distribution of emulsions. They present results for a two-step process where they used a bicontinuous microemulsion phase. A pre-concentrate consisting of oil and emulsifiers with a water content of 15 % w/w was emulsified at 85°C. In a subsequent dilution step with water at 40°C, the desired emulsion was formulated. This preparation method yielded a fine-disperse emulsion with a mono-modal droplet distribution of approximately 110 nm [Buchannan, 1995].

1.2.2.5 Myelinic figures and liquid crystal explosion

Myelinic figures are long tubules of the lamellar liquid crystal phase. Rang et al. [1996] studied the intermediate phase formation and other dynamic behavior which occurred when drops containing mixtures of n-decane and a short-chain alcohol were contacted with dilute solutions of an amine oxide surfactant. They described that in their contacting experiments one of the first intermediate phase formed was the lamellar liquid crystal. This intermediate phase grew very rapidly for systems rich in hydrocarbon as short and fluid myelinic figures containing substantial amounts of both hydrocarbon and

water appear. These figures almost immediately disintegrated into a multitude of drops in a process resembling an explosion (see Figure 1-8). For systems rich in long chain alcohol, a highly viscous lamellar phase developed around the drop in a configuration resembling a polyhedron.
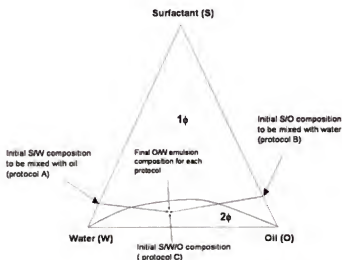
Figure 1-7. Schematic representation of the experimental path of three emulsification protocols (A) addition of decane to water/surfactant mixtures, (B) addition of water to n-decane/Brij30 solutions, and (C) mixing of surfactant, oil, and water [Forgiarini, 2001].

Figure 1-8. Myelinic figures and liquid crystal explosions.

The work presented by McBain and Woo [1937] for water-diglycol laurate system evidently depicts myelinic figures as well. Some other reports of spontaneous emulsification involving emulsified liquid crystals or, at least, formation of an intermediate liquid crystal layer between the phases initially contacted are those of systems where a slightly polar compound such as a long-chain alcohol or a solution of such a compound or a surfactant in a hydrocarbon is contacted with water or an aqueous surfactant solution. Figure 1-6 presents a picture of classic myelinic figures [Saupe, 1977].

1.3 Phase Behavior Diagrams

Phase Diagrams are well known for being a key tool for equilibrium phase analysis, and recently have become important for designing emulsion protocol. Although equilibrium phase behavior diagrams cannot completely reveal the true nature of the interfacial disruption which gives rise to spontaneous emulsification, they at least allow (a) the prediction of the phase structures which are the most likely to form when an oil phase is brought in contact with an aqueous solution [Miller, 1988; Ruschak, 1972], and (b) the determination of phases which play the key role in the spontaneous emulsification process [Kunieda, 1996; Ozawa, 1978].

Pouton [1997] indicates that in practice phase behavior can be correlated with the disruption of the oil-water interface caused by penetration of water into the oil phase or by diffusion of co-solvents away from the oil phase. The precise spontaneous emulsification mechanism remains the subject of speculation (as presented in section 1.2) but there is an empirical link between spontaneous emulsification phenomenon, liquid crystal formation, oil-water phase inversion temperature and enhanced solubilization of water by oil formulations [Pouton, 1997].

The simplest systems in which spontaneous emulsification occurs are certain ternary systems consisting of water, a hydrocarbon, and a short-chain alcohol or fatty acid. Phase behavior of three component systems like this, are often represented by isothermal triangular phase diagrams such as that presented in Figure 1-9. The ternary system consists of a single-phase region (1φ) and two-phase region (2φ) where aqueous and oil phases coexist, and as one changes the alcohol by a surfactant the presence of more phases would be observed, as shown in Figure 1-10.
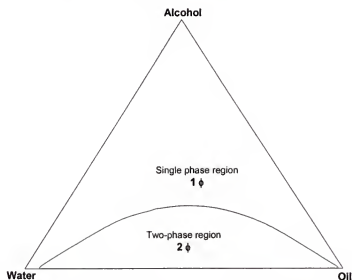
Figure 1-9. Sketch of a triangular phase diagram for a simple system (water-alcohol-oil).

Pouton [1997] explains that triangular phase diagrams are also a good representation of the phase behavior of more complex systems that could be expected for mixtures involving oils, aqueous salty solutions, surfactants and co-surfactants. (One should notice that diagrams of this kind would be a triangular representation for pseudo-components since there are no longer only three components). In such systems, some areas of the phase diagram are occupied by mixtures that form pure phases of swollen micellar solutions, bicontinuous microemulsions or liquid crystal phases, while in others

regions more than one phase coexist (if the oil is less polar, then the incidence of association structures formed as a single phase is reduced, so that large areas of the phase diagram would be multiphasic).

The use of phase diagrams has been correlated with the diffusion and stranding mechanism (by means of the diffusion path theory), the sequential change in structures by temperature change mechanism, and the sequential change in structures by concentration gradient mechanism.

Finally, it is important to mention that some spontaneous emulsification mechanisms cannot be correlated with the use of phase diagrams. Specifically, those systems in which emulsions form via negative interfacial tension mechanism or interfacial turbulence mechanism (see section 1.2) cannot be appropriately described by the phase diagrams since the instabilities observed in them are more related to dynamic processes than to thermodynamic conditions.

1.3.1 Diffusion Path Theory

The diffusion path theory is a mathematical-physical model able to predict spontaneous emulsification and some other features related with this phenomenon. This theory, presented originally by Ruschak and Miller [1972], considered the solution of the diffusion equations for semi-infinite phases with certain simplifying assumptions and predicted only the initial behavior to be expected when non-equilibrium phases are brought in contact. Since it assumes semi-infinite phases, it is limited to times for which some portions of both phases contacted retain their initial compositions. Furthermore, it does not consider coalescence of the drops formed.

Because all the diffusion coefficients are the same for all phases, the set of compositions in the system is independent of time and can be plotted directly on the ternary phase diagram. This graphic representation is the so-called diffusion path.
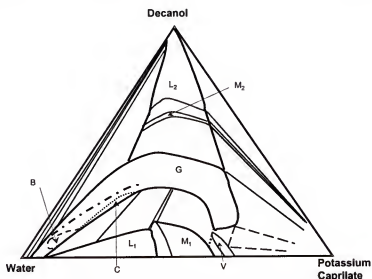
Figure 1-10. Example of an equilibrium phase diagram for a complex system. The system is potassium caprylate-decanol-water at 20°C. L_1, isotropic aqueous solution; L_2, isotropic oil solution; B, lamellar phase (mucous woven type); G, lamellar phase (neat phase); C, tetragonal phase; M_1, hexagonal phase (middle phase); M_2, inverse hexagonal phase; V, cubic phase [Pouton, 1997].

For simple systems the diffusion path consists of two segments representing the compositions in the aqueous and oil phases, respectively, as illustrated in Figure 1-11. If the diffusion coefficients of all three components are equal in any phase, then all possible compositions for that phase will lie along a straight line. Since one of the assumptions of the analysis is local equilibrium at the interface, the ends of the two segments which represent interfacial compositions lie at the ends of a tie-line (see Figure 1-11).

In some cases, one or both segments pass through the two-phase region (2ϕ) of the ternary diagram (e.g., the segment A-B in Figure 1-11). That is, even though both initial compositions are in the single-phase region (1ϕ), some of the intermediate

compositions predicted by the analysis are supersaturated. Ruschak and Miller [1972] proposed, and then confirmed experimentally in several systems, that spontaneous emulsification occurred when such local super-saturation was predicted. They were able to predict not only whether emulsification would occur but also in which phase. For instance, the diffusion path of Figure 1-11 predicts emulsification in the aqueous but not in the oil phase. They noted that a condition for emulsification is the presence of a component able to diffuse from a bulk phase in which it is less soluble into the bulk phase in which it is more soluble. Several other examples of the diffusion path theory (e.g., more complex systems comprising alcohols, and surfactants) can be found in the work of Miller [1988] or in a review published by Lopez-Montilla et al. [2002a].
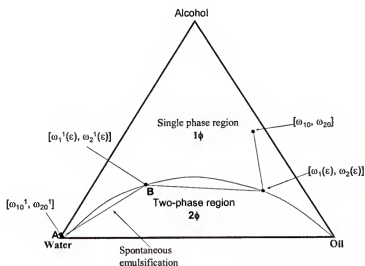
Figure 1-11. Triangle phase diagram in which a two-phase diffusion path is depicted. The alcohol has equal diffusion coefficients in each phase [Ruschak, 1972].

1.3.2 Spontaneous Emulsification Due to Temperature Gradient

Ozawa et al. [1997] built the phase diagram for the 0.1 M NaCl aqueous solution/$C_{12}EO_6$/monolaurin/n-decane system at different temperatures (ranging from 0 to 50°C) and explained that in this system highly concentrated o/w emulsions are

spontaneously formed by a rapid decrease in temperature through sequences of self-organizing structures. Similarly, Kunieda et al. [1996] built the phase diagram for the 0.1 M NaCl aqueous solution/$C_{12}EO_4$/n-decane system in the same temperature range as before and explained that in such systems highly concentrated w/o emulsions are spontaneously formed by a rapid increase in temperature through sequences of self-organizing structures (see section 1.2.2.3).

In both cases, the sequential changes in the structures were indirectly monitored by means of electric conductivity and the results were interpreted on the basis of phase behavior. The phase behavior analysis from the phase diagrams obtained for both systems revealed that (a) the spontaneous curvature of the surfactant molecular layer changes from concave to convex toward water with decreasing temperature (see Figure 1-12 and 13), and (b) the spontaneous curvature of that layer changes from concave to convex toward oil with increasing temperature (see Figure 1-14 and 1-15). Solans and Kunieda et al. [1996] and Ozawa et al. [1997] explain that it is important to lower/increase the temperature quickly to form stable highly concentrated emulsions with fine droplets, because the systems pass through an extremely unstable emulsion region, which corresponds with the HLB temperature.

As a comment for this section, it is important to point out that when a system like the ones studied by Kunieda et al. [1996] and Ozawa et al. [1997] reaches the homogeneous L_3 single phase, it completely loses the memory of the previous phase transformations, so that what is actually important for the spontaneous emulsification under this mechanism is the occurrence of this L_3 phase.

The following is a detailed description of the correlation of this mechanism with the phase diagrams:

1.3.2.1 Formation of highly concentrated o/w emulsions by decreasing temperature

Ozawa et al. [1997] indicate that w/o microemulsions with compositions corresponding to path A in Figure 1-12 were quickly cooled to a temperature at which the two-phase region [2ϕ; L_1 (micellar solution phase) plus O (oil phase)] appears. Similarly, with compositions corresponding to path B, phase regions including lamellar liquid crystals (L_α) appear after quickly cooling the system. At composition B, the bulk oil phase is separated and emulsification is not completed. On the other hand, at composition A, no drainage is observed, and white and viscous o/w emulsions are formed at a temperature lower than that of the single-phase microemulsion. Thus, it is considered that if the cooling speed is fast, the system passes the unstable emulsion region in a short time and the coalescence of oil droplets does not progress.

Ozawa et al. [1997] suggest that at composition A in Figure 1-12 the spontaneous curvature of surfactant molecular layers continuously changes from convex toward oil to convex toward water while cooling. The change in self-organizing structures is schematically shown in Figure 1-13, where it can be seen that they change from a reverse micellar w/o microemulsion to an o/w emulsion via the surfactant phase (D phase), L_α phase, and the bicontinuous sponge phase (L_3 phase,) with the decrease in temperature. Whereas the surfactant phase (D phase) and L_α phase coexist with the oil phase, the bicontinuous L_3 phase is present as a single phase. The existence of this single L_3 phase region is the key for the spontaneous emulsification process [Forgiarini, 2001]. On the other hand, at composition B, L_α phase is formed since the water content is not sufficient

to form a bicontinuous L_3 phase or aqueous micelles (see Figure 1-12). In this case, the

curvature of surfactant molecular layers is flat to water at the final temperature, (i.e.,

HIPREs are not formed). Based on this, Ozawa et al. [1997] concluded that, in addition

to the quick temperature drop, the surfactant to brine ratio is another important factor in

spontaneous formation of emulsions for this specific system and mechanism.
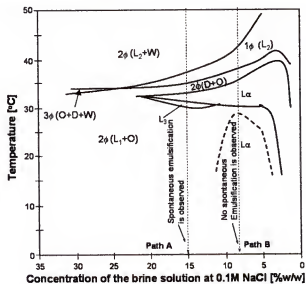
Figure 1-12. Phase diagram of the 0.1 M NaCl aq./$C_{12}EO_6$/monolaurin/n-decane system as function of temperature. The $C_{12}EO_6$:monolaurin:n-decane ratio is kept constant at 3.5:1.5:95. The weight percentage of 0.1 M NaCl aq. in the system is plotted horizontally. L_2, w/o microemulsion; L_1, o/w microemulsion; D, middle-phase microemulsion; L_3, bicontinuous surfactant phase; L_α, lamellar liquid crystal; W and O, excess water and oil phases, respectively. 1ϕ, 2ϕ, and 3ϕ indicate one-, two-, and three-phase regions respectively [Ozawa, 1997].

1.3.2.2 Formation of highly concentrated w/o emulsions by increasing temperature

To study this process, Kunieda et al. [1996] shifted quickly the temperature of a

single microemulsion from 10 to 20 and 50°C. In both cases, they observed the

formation of w/o emulsions. The sample with final temperature of 20° was less viscous

than that with final temperature of 50°; Kunieda [1996] determined that the emulsion

droplets in the former sample are larger once they have been allowed to cool down to

room temperature. When the temperature change is slow, it is possible that water droplets are coalesced in the two-phase region (2φ) including L_3 and excess water (see Figure 1-14).
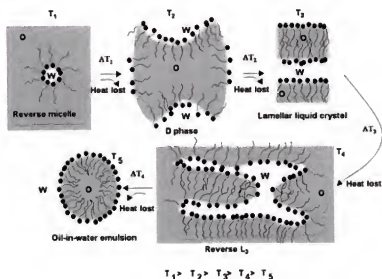
Figure 1-13. Schematic of the change in self-organizing structures during spontaneous formation of highly concentrated o/w emulsions. W and O represents water and oil, respectively [Ozawa, 1997].

The hydrophilic-lipophilic balance property of the polyoxyethylene-type nonionic surfactant is changed from hydrophilic to lipophilic by increasing temperature, which in turn varies the spontaneous curvature of the surfactant self-organizing structure from concave to convex toward oil. Figure 1-15 shows the schematic change in shape of self-organizing structures during spontaneous formation of highly concentrated emulsions. In a single L_1 phase region, oil-swollen micelles are present and no excess oil phase is separated. When vesicles are formed, some water is trapped in the vesicles and the vesicular size is much larger than micelles.

Kunieda et al. [1996] explain that in the lamellar liquid crystal most of the water is trapped in the bilayer network. Therefore, the water-swollen lamellar liquid crystal

spontaneously forms by simple temperature change. When the curvature of the surfactant layer becomes flat and vesicles are merged to the lamellar liquid crystal, most of the water is spontaneously taken up in the surfactant layers. However, with the increase in temperature, the bilayer becomes flexible and the phase transition from L_α to L_3 phase occurs. When the system enters the single L_3 phase, the curvature of the surfactant molecular layer is considered to be slightly concave toward water, as is shown in Figure 1-14. According to Kunieda et al. [1996], this means that water is trapped in the flexible surfactant bilayers and micro-water domains are formed in this phase. Since surfactant bilayers are more flexible in the L_3 phase, the micro-water domains may be quickly connected to and disconnected from each other.
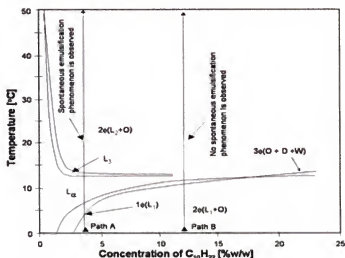
Figure 1-14. Phase diagram of the 0.1 M aqueous NaCl/$C_{12}EO_4$/decane system as a function of temperature. Decane was added to 3 % w/w $C_{12}EO_4$ aqueous solution, and the weight percent of decane in the system is plotted horizontally. L_2, w/o microemulsion; L_1, o/w microemulsion; D, middle-phase microemulsion; L_3, bicontinuous surfactant phase; L_α, lamellar liquid crystal; W and O, excess water and oil phases, respectively. 1ϕ, 2ϕ, and 3ϕ indicate one-, two-, and three-phase regions [Ozawa, 1997].

Finally, Kunieda et al. [1996] explain that when the single L_3 phase is changed to the L_3 + W region, the excess water phase is separated from the L_3 phase due to the

coalescence of water droplets. If the temperature changes fast enough, the system does not feel the existence of the temperature unstable region; then, the coalescence of water droplets does not proceed and, subsequently, the macroscopic phase separation does not occur in the two-phase region (2φ). Therefore, it is very important to change temperature quickly in order to form fine concentrated stable emulsions.
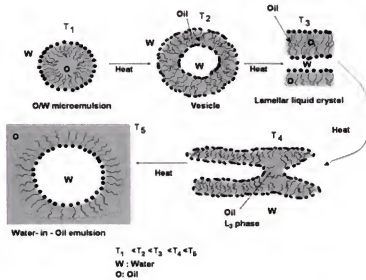
Figure 1-15. Schematic change in spontaneous curvature of surfactant layers in the process of spontaneous formation of gel-emulsions [Kunieda, 1996].

1.3.3 Spontaneous Emulsification Due to Concentration Gradient of Components

The phase diagram made by Forgiarini et al. [2000, 2001] for the water/Brij30/n-decane system at 25°C is shown in Figure 1-16. They explain that although the surfactant used in their experiments is of technical grade and the Gibbs phase rule does not apply to this pseudo-ternary system, the general features of the phase behavior of this system agree with those of typical ternary water/polyoxyethylene-alkyl-ether-nonionic surfactant/oil systems.

Three distinct single-phase regions (1φ) are observed in Figure 1-16 (a) an isotropic region, L_2, along the oil-surfactant axis, (b) a shear birefringent region, D', and

(c) a lamellar liquid crystal region, L_α, extending from the water-surfactant axis toward the oil vertex. The rest of the diagram consists of several two- and three-phase regions.

According to Kunieda et al. [1985, 1991], the structure of compositions in the L_2 phase region would correspond to inverse micelles or w/o microemulsions whereas that of region D' would correspond to a bicontinuous or sponge-type structure (so-called L_3). At low surfactant concentration, a miscibility gap, consisting of two liquid phases (an aqueous and an oil (L_1 + O) phase), exists along the water-decane axis. On the other hand, at higher surfactant concentration, the two-phase region denoted as (D' + $L\alpha$) consists of a lower liquid birefringent phase in equilibrium with an upper lamellar liquid crystal phase.

Forgiarini et al. [2000, 2001] could measure interfacial tensions only for samples belonging to region (L_1 + O) at 5 % w/w of surfactant. For this system, they observed that the interfacial tension value drops about 2 orders of magnitude from 2.67×10^{-1} mN/m to 6.5×10^{-3} mN/m when the value of the oil weight fractions (S) changes from 0.8 to 0.3. For S = 0.3 the hydrophilic-lipophilic-balance temperature (T_{HLB}) was very close to 25°C, which was the experimental temperature. In previous studies, the requirement for low values of interfacial tensions for nano-emulsion formation had been the subject of debate [El-Aasser, 1988; Rosano, 1987]; however, nano-emulsion formation cannot be fully explained by the equilibrium properties, since low interfacial tensions are probably necessary but not sufficient to explain nano-emulsion formation.

Nano-emulsions can be produced, depending on the order of addition of the components, in compositions showing a phase equilibrium consisting of aqueous, lamellar liquid crystal, and oil phases and similar low interfacial tension values.

Consequently, the key factor should be attributed to the kinetics of the emulsification process. To probe that, Forgiarini et al. [2000, 2001] performed the emulsification process with high energy input using a high-energy device at high rpm, and obtained a nano-emulsion only above 15, 000 rpm.

1.4 Theoretical Approaches to Describe Some Aspects of Spontaneous Emulsification

Theoretically, some aspects of the spontaneous emulsification phenomena have been addressed by Granek et al. [1993], Sorensen [1978], Theissen and Gommper [1999], Gommper and Schick [1994], and Ruschak and Miller [1972]. Nevertheless, this aspect of the spontaneous emulsification phenomenon escapes from the scope of this dissertation. Lopez-Montilla et al. [2002a] made a comprehensive review of these works.

1.5 Applications

Spontaneous emulsification has established itself as a very important technological tool in several fields, not to mention the wide variety of potential applications that it has. Some examples of applications of this phenomenon are (a) formation of an emulsion on site for agricultural applications, (b) development of new and improved detergents, (c) improvement of drug delivery systems, (d) optimization of food production, (e) lubricant oils for specific use, (f) development of new and improved techniques for enhanced oil recovery, (g) production of nano-emulsion at low energy consumption, etc [Forgiarini, 2001; Nishimi, 2001; Ozawa, 1997; Shahidzadeh, 1993].

1.5.1 Pesticides, Insecticides and Herbicides

Many agricultural products (e.g., pesticides, insecticides and herbicides) consist or oils that must be diluted in water before use. When diluted, they must not only disperse easily without much agitation and form an emulsion of adequate stability, but

also keep their characteristics until they are used. Therefore, self-emulsifying oils are then highly suitable as vehicles for agricultural products since as low as 1 % w/w of them are required to prepare the proper mixture and to spare the manufacturers the transport of water to the farm from the industrial facility, which is both unnecessary and expensive. Accordingly, the active ingredient of these products is then formulated in an anhydrous oil (containing surfactants) which is conveniently transported. The oil concentrate can then be added to water from a local supply and sprayed at the point of application.
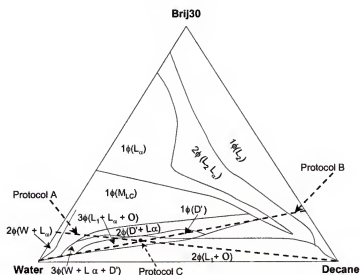
Figure 1-16. Phase behavior of water/Brij30/decane system at 25°C L_2, isotropic liquid phase; L_{α}, lamellar liquid crystal phase; D', shear birefringent liquid phase; L_1, bluish liquid phase (o/w microemulsion); W, aqueous liquid phase; O, oil liquid phase; MLC, multiphase region including lamellar liquid crystal [Forgiarini, 2001].

Another critical feature of these anhydrous formulations is their ability to form suitable emulsions with a variety of natural waters, in spite of their hardness [Groves, 1978].

An example of the relevance that self-emulsifying systems have had in the pesticide industry is the well known (and now proscribed) DDT. To formulate DDT as

self-emulsifying oil in xylene, both hydrophilic and hydrophobic surfactants were required which had to be, at the same time, soluble in the oil solvent. The surfactants had also to be in a definite ratio or balance with each other [Groves, 1974].

1.5.2 Detergency

Rosen [1972] defined detergency as cleaning power. According to this concept, when the term detergency is applied to surface-active agents it means the special property it has of enhancing the cleaning power of a liquid. This is accomplished by a combination of different effects involving (a) adsorption of surface-active agents at interfaces, (b) lowering of the interfacial tension, (c) increasing of solubilization, (d) emulsification, and (e) formation and dissipation of interfacial charges.

In every cleaning process three common elements are present (a) the substrate, (i.e., the surface that is to be cleaned), (b) the soil (i.e., the material that is to be removed from the substrate in the cleaning process), and (c) the cleaning solution or bath. It also requires mechanical work in the process to finally remove the soil from the substrate.

Solubilization has long been known to be a major factor in the removal of oil soil and its retention by the bath. This is based upon the observation that oil (soil) removal from both hard and textile surfaces becomes significant only above the CMC for nonionic and even for some anionic surfactants having low CMCs, and reaches its maximum only at several times the CMC. The extent of solubilization of the oil (soil) depends on the chemical structure of the surfactant, its concentration in the bath, and the temperature, and others factors such as alcohol and salt concentration [Rosen, 1972; Salager, 1999].

When insufficient surfactant is present to solubilize all the oil (soil) in micelles, the remainder is probably suspended in the bath by macro-emulsification. For macro-emulsification to be important, it is imperative that the interfacial tension between oil

(soil) droplets and bath be low or that a favorable condition for spontaneous emulsification must exist. Spontaneous emulsification has been found to become a major factor when alkaline builders are added to a cleaning bath containing polyoxyethylene (POE) nonionic surfactant and the soil was mineral oil containing 5 % w/w oleic acid.

Spontaneous emulsification has been proposed as one of the possible mechanisms for the removal of liquid soils from a substrate. According to the detergent used and the conditions of the process, the liquid soil could be spontaneously emulsified by a process described by one or several of the spontaneous emulsification mechanisms described above; once this liquid soil is emulsified and dispersed into the water, it can be easily removed from the substrate with low mechanical energy requirements.

Finally, it is worthwhile to mention that it is considered that in the near future, spontaneous emulsifications will be an important factor in the design of new and improved detergents that, for example, may work at low temperature (15 to 35°C) and with low energy requirements [Raney, 1987].

1.5.3 Skin-care Products

Skin is the largest organ of the body and plays a critical role as the interface between the human body and the environment. However, skin can only be effective as a barrier if it is intact. Simion et al. [1998] explain that hand and body lotions play a vital role in helping to maintain the integrity and plasticity of the skin in the face of many outside threats. Furthermore, they mention that such lotions provide a crucial benefit to consumers in improving the feel of their skin and eliminating the negative sensations of dryness and itching associated with dry skin. Nowadays, skin is exposed to a number of threats such as shifting demographics, increased usage of low humidity central heating and air conditioning systems, household detergents, personal cleansers, among others.

These treats cause a dramatic decrease in the skin's ability to act as a barrier. Simion et al. [1998] explain that hand and body moisturizers have been designed to provide relief to dry skin sufferers by increasing the plasticity of the skin while eliminating skin scaling, and to act as vehicles for active ingredients (such as sunscreens and cosmetically active compounds).

According to Simion et al. [1998] the first ingredient in most hand and body lotions is water, which typically makes up 70 % w/w or more of the formula. Water has two important functions (a) it is the vehicle by which many other ingredients are delivered to the skin, and (b) it hydrates the skin for a short time before evaporating.

Second in the ingredient list usually come the emollients. Historically, lanolin was one of the first emollients used widely by industry, since it provides a strong occlusive effect when applied to skin, and may also directly plasticize it. However, due to some adverse reactions that a number of people have to Lanolin, it has largely been replaced by other emollients with similar occlusive effect on the skin and with equivalent observable skin dryness reduction. Among these emollients are mineral oil, petrolatum, triglycerides and silicones.

After the emollients one usually finds the humectants and the emulsifiers in the ingredient list of a lotion. The most common humectant is glycerin (glycerol), but other lotions may include sorbitol, propylene glycol, dipropylene glycol and butylene glycol. Emulsifiers are key ingredients that are used to stabilize the lotions by retarding the natural tendency of oils and aqueous phases to separate. Many types of emulsifiers are used, and it is quite common for a lotion to include three or more emulsifiers to provide the desired stability. Mono- and diglycerides derived from natural fats and oils, and fatty

acids (especially stearic acid) are effective emulsifiers when converted to soaps. Fatty alcohols, also derived from triglycerides, are widely used as emulsifiers and viscosity builders in this kind of cosmetic products.

Finally, in order to provide additional emulsion stability and contribute to the desired consistency of a hand and body lotion, high molecular-weight polymers are ingredients often used to increase the viscosity of the formula. There are some minor components which are preservatives, fragrances and skin-care additives, as well.

It is worth noting that since many of the ingredients used in hand and body lotions are complex chemical entities, a standard nomenclature has been developed by the Cosmetics, Toiletries, and Fragrance Association (CTFA). Under CTFA guidelines, manufacturers are obliged to use the assigned "International Cosmetic Ingredient" (INCI) name for all ingredients used in their products.

Regarding the hand and body lotions structure, Simion et al. [1998] indicate that most lotions are emulsions of oil- and water-soluble materials, and that the way the ingredients are distributed between the oil and aqueous phases plays a significant role in how they are delivered to and partition into the skin; this in turn affects their moisturizing effects, and the feel of the skin during and after application.

Emulsions for hand and body are formed consisting of tiny droplets which give an additional kinetic stability to the lotion, and can be further characterized as being one of two emulsion types w/o or o/w emulsions, with the o/w being the most common in this area of application by far.

In the o/w emulsion used in hand and body lotions, the water insoluble ingredients (oils) are the emollients, which are typically used in the range of 5 to 25 % w/w of the

total formula, and the fragrance. Water together with all of the soluble ingredients (e.g., humectants) forms a solution into which the water insoluble ingredients are dispersed. Emulsifiers stabilize the formula by coating each oil droplet and preventing it from coalescing with other oil droplets and thereby growing in size. Preventing growth in droplet size is critical for stabilizing an emulsion. The appearance of large droplets would compromise the lotion's smooth texture and appearance.

In terms of aesthetics, o/w hand and body lotions can range from very "light" (low oil content) to "heavy" (high oil content). The skin feel of the product during rub in and after drying is affected not only by the amount of oil, but also the composition of the emollient oils used in the formula. For example, if the oil phase is composed mainly of mineral oil, the lotion will generally provide an "oil" feel on the skin, while the use of emollients like lanolin or petrolatum gives a heavier "greasy" skin feel.

Finally, o/w emulsions may be better able to deliver water soluble materials to the skin; for example, they have enhanced delivery of lactic acid to the skin.

Simion et al. [1998] indicate that the w/o emulsions are much less common than the o/w type for several reasons. The most important reason is probably aesthetics. In order to have enough emollient oil to surround the water, a relatively large percentage of oil is required, usually in excess of 25 %. Thus it is very difficult to formulate a w/o hand and body lotion with a light skin feel. Another reason why w/o emulsions are not common is that they are more expensive to manufacture. Oils are more expensive than water, and increasing the oil content will increase formula cost. Additionally, in order to produce and stabilize w/o emulsions, special emulsifiers are necessary, which generally cost more than o/w emulsifiers.

In addition to the binary emulsion systems already discussed, Simion et al. [1998] include some more complicated emulsions that have been developed for use in personal care products. One such system is the W/o/w emulsion, where a water phase is first dispersed and stabilized into an oil phase; this initial w/o emulsion so formed is in turn dispersed into a second water phase. The purpose of this elaborate emulsion structure is to protect water soluble ingredients, which are sequestered inside the oil phase, where they will not come into contact with other ingredients in the second water phase that may degrade them. Examples of ingredients that might require such protection are biological materials such as enzymes.

1.5.4 Drug Delivery Systems: Lipid Formulations for Oral Administration

The potential of self-emulsifying drug delivery systems has been evident with both the marketing of Cyclosporine A, Ritonavir and Saquinavir (the latter two known as HIV inhibitors) [Pouton, 1997; Pouton, 2000] and the many references which show the beneficial effects of food or oils on bioavailability of hydrophobic drugs. The pharmaceutical products, for example show that lipids and surfactants are crucial to the success of the production of water immiscible drugs.

The earliest reports of self emulsifying systems using pharmaceutical materials were of pastes, based on waxy alcohol ethoxylates [Groves, 1976]. These systems do disperse to form fine o/w emulsions but since there is not any advantage in using waxy pastes, they are not used anymore. Nowadays, as a general rule it is sensible to use the simplest effective formulation, restricting the number of excipients to a minimum.

Pouton [1997, 2000] explains that "lipid" formulations for oral administration of drugs generally consist of a drug dissolved in a blend of two or more excipients. The primary mechanism which leads to improved bioavailability is usually avoidance of the

slow dissolution process which limits the bioavailability of hydrophobic drugs from solid dosage forms. Ideally the formulation allows the drug to remain in a dissolved state throughout its transit through the gastrointestinal tract.

The availability of a drug for absorption can be enhanced by presentation of the drug as a solubilizate within a colloidal dispersion. This can be achieved in principle by formulation of the drug in a self-emulsifying system or alternatively by taking advantage of the natural process of triglyceride digestion. In practice lipid formulations range from pure oils to blends which contain a substantial proportion of hydrophilic surfactants or co-solvents (i.e., "lipid" formulations are a diverse group of formulations which have a wide range of properties that result from the blending of up to five classes of excipients pure triglyceride oils, mixed glycerides, lipophilic surfactants, hydrophilic surfactants and water-soluble co-solvents).

All excipients have certain advantages and disadvantages. A main concern is the toxicity of the excipients, since only limited data is available on their acute and chronic toxicity. A second issue is the solvent capacity of the formulation, which may not be high enough for a certain drug.

Under optimum conditions it is possible to formulate a "self-emulsifying drug delivery system" (SEDDS) which emulsifies in aqueous solutions under very gentle conditions of agitation, to result in a dispersion of colloidal dimensions [Wakerly, 1986]. The following are some detailed lipid formulations, presented to clarify the role of spontaneous emulsification.

If the surfactant is insufficiently hydrophilic (i.e., HLB <12) to be dissolved and form micelles in aqueous solution, then it will form a dispersed phase, either with or

separated from the oil components. This type of formulation is likely to retain its solvent capacity for the drug after dispersion and is referred to as Type II in drug delivery literature [Groves, 1997; Pouton, 2000]. The distinguishing features of Type II systems are an efficient self-emulsification, and the absence of water-soluble components, and the formulation comprises medium chain triglycerides and/or mono- or diglycerides, and ethoxylated oleate esters with HLB values of approximately 11. As the surfactant content in the blend is increased there is a threshold at approximately 25 % w/w surfactant beyond which self-emulsification occurs. At higher surfactant concentrations (i.e., concentrations greater than 65 % w/w depending on the materials) the progress of emulsification is compromised by viscous liquid crystal gels which form at the oil-water interface. If homogenized, these mixtures would produce very stable emulsions, but they require energy to break up the particles and in practice are not self-emulsifying systems. As a practical example, Type II systems consisting of medium chain triglycerides and polyoxyethylene-(25)-glyceryl trioleate (Tagat TO) have been reported to produce particles as fine as 100-250 nm by self-emulsification, depending on the surfactant concentration [Pouton, 2000].

Hydrophilic surfactants (water soluble with HLB > 12) and/or water-soluble co-solvents have also been blended with oils to produce self-emulsifying systems. When the surfactant content is high (for example 40 % w/w or more) or co-solvents are included in addition to surfactants, it is possible to produce very fine dispersions (< 100 nm in diameter) under conditions of gentle agitation [Constantinides, 1995]. These hydrophilic surfactants or water-soluble co-solvents (such as propylene glycol, polyethylene glycol, ethanol, etc.) also increase the solvent capacity of the formulation for certain drugs.

Then, the difference between these and the Type II formulations is that the water-soluble components will tend to partition from the oil during dispersion, and become dissolved in the aqueous phase. The result of this phase separation, which is in fact the driving force for emulsification by the Diffusion and Stranding mechanism (see section 1.2.1.2), is that the system loss its solvent capacity. Consequently, the drug is partially precipitated when the formulation disperses; the extent of this precipitation will depend on the physical chemistry of the drug and how hydrophilic the formulation is. Formulations which include water-soluble components are referred to as Type III formulations, and are referred to as "self-micro-emulsifying" systems, due to the optical clarity which can be achieved with Type III systems. As the chance of precipitation is greater (usually when the formulation contains a higher proportion of hydrophilic components), Type III formulations are arbitrarily split into Type IIIA and Type IIIB, to help identify very hydrophilic (Type IIIB) formulations. (A reader interested in applied formulations is referred to the following two references. The first is the work of Kommuru and et al. [2001], who developed self-emulsifying drug delivery systems (SEDDS) of coenzyme Q10, using polyglycolyzed glycerides (PGG) as emulsifiers to evaluate their bioavailability in dogs. The second was done by New and Kirby [1997], who explain a technique that they developed to allow encapsulation of water-soluble macromolecules in oil without the intermediary of a two phase system).

1.5.5 Food Products: Mayonnaise and Salad Dressings

Mayonnaise is a very stable o/w emulsion (i.e., it can be stored several years without breaking) made from vegetable oil, vinegar, salt, and spices. It is emulsified with egg yolk and thickened. Salad dressings are also o/w emulsions of oil and vinegar, which may contain other flavorings and be as stable as mayonnaise. The FDA defines salad

dressing as a semisolid emulsified food with the same ingredients and optional ingredients as mayonnaise with the exception of the inclusion of a cooked or partially cooked starch paste. Thus, the basic ingredients of salad dressing are acetic acid, salt, sugar, water and vegetable oil. Salad dressings were originally developed as a commercial substitute for mayonnaise in the mid-nineteenth century [Bender, 1995].

Examples of salad dressing are (a) red mayonnaise, which is prepared by adding beetroot juice and the coral (eggs) of lobster to mayonnaise and is an accompaniment to lobster and other seafood dishes; (b) Russian dressing, which is made from mayonnaise with pimento, chili sauce, green pepper, and celery, or sometimes by mixing mayonnaise with tomato ketchup, (c) Thousand Island dressing, which is made from equal parts of mayonnaise and Russian dressing with whipped cream, and (d) French dressing (vinaigrette), which is a temporary emulsion of oil and vinegar and is stabilized with pectin or vegetable gum.

There are two types of salad dressing, pourable and spoonable. (The original spoonable dressing was mayonnaise). These two types of salad dressings vary in flavor, chemical and physical properties (especially viscosity). The pourable dressing may either be sold in a homogeneous phase or in two phases; the two-phase salad dressings will require shaking prior to use. The typical pH of these products ranges from 3.5 to 3.9. However, spoonable salad dressings contain less acid than the pourable salad dressings, causing less microbial stability; nevertheless, preservatives are used in both salad dressing types. The primary preservatives used to control microbial spoilage are sodium benzoate and or potassium sorbate [Bender, 1995].

The production of a salad dressing requires the use of a colloid mill or a homogenizer to mix the ingredients. The colloid mill uses the shear and turbulence of liquid passing between two cylindrical surfaces (a rotor and a stator) that are closely spaced and is used to mix high viscosity materials. A pressure homogenizer, on the other hand, is used to mix lower viscosity materials; the ingredients of the fluid are thoroughly mixed when it passes through an orifice at high pressures and speeds. It is important to stress the fact that both of these processes are high energy consuming. Prior using the colloid mill or homogenizer, the vinegar, salt, starch and water are heated to approximately 90°C. Once a starch paste has formed, this mixture is cooled and then eggs, sugar, spices and oil are added. This mixture is then passed through the colloid mill or the pressure homogenizer prior to packaging.

The mayonnaise and salad dressings are a good example where the self-emulsification process could be useful for the food industry. As mentioned above, they are traditionally made applying a vigorous mixing where mechanical energy is used to convert films of oil into droplets (which are then dispersed in yoke and vinegar). Nevertheless, Shahidzadeh et al. [1999] suggested that they can also be formed by a self-emulsification process with the convenient low energy consumption and a small particle size distribution.

According to Shahidzadeh et al. [1999], the mayonnaise is stable due to the tensoactive molecules present in the yoke. These tensoactive molecules decrease the interfacial tension between oil and water by a factor of 10, 000, which strongly affect the energy required to disperse one into the other. Shahidzadeh et al. [1999] indicate that this self-emulsification process is described by the explosion of vesicles by osmotic pressure

difference mechanism (which is explained in section 1.2.2.1). (A reader interested in mayonnaise and salad dressing technology will find the following web site interesting: http://www.orst.edu/food-resource/misc/emulsio.html).

1.5.6 Lubricant Oils for Specific Applications: Cutting-fluids

Besides the well-known lubricant oils and greases for industrial and automotive applications, it is common to find specific lubricants for particular applications. Some formulations of these lubricants are obtained with systems that present self-emulsification.

Cutting-fluids are liquids that are used for machining processes. These cutting-fluids generally contain about ten products and their formulations are almost empirically developed, and are marketed under the form of concentrates that the user has to dilute with water before use. One type of these systems is the aqueous cutting-fluids, which consist essentially of mineral oil, anionic surfactant, nonionic surfactants and sometimes water. In these systems the water-oil ratio is variable, and the amount of surfactant is minimized to reduce costs. Moreover, for stability conditions and easiness of use, it is convenient that the concentrates should be monophasic microemulsions [Bataller, 2000].

The main characteristics of the cutting-fluids are their capability to work as a heat removal means and a lubricant. Unfortunately, water or oil alone cannot perform both these functions at the same time. Therefore, a combination of a cooling agent and an oil lubricant is required. The combination of water and oil with a surfactant is the best choice for the cutting-fluids, since water is a good cooling agent due to its high specific heat, conductivity and vaporization heat and oil is a good lubricant agent. Dilutions of these systems always make o/w emulsions, and their appearance may vary from a whitish color to a bluish color. The droplet size after dilution depends, among other factors, on

the formulation of the concentrate and often also on the hardness of the water added by the final user [Bataller, 2000].

During the machining process (e.g., met al/turning, milling, drilling) a tool comes in contact with a metallic piece and cuts it in order to modify its shape. Rubbing and friction during contact and met al tearing off cause the temperature to rise up in the cutting-zone. It is fundamental to reduce this temperature and to minimize friction in order to avoid any irreversible damage to both the met al piece and the tool [Bataller, 2000].

The cutting-fluid emulsions become unstable under shear and heat in specific industrial applications (mainly those of mechanical fabrication of delicate pieces such as gears in lathes and milling machines). When poured over the cutting surface during the machining operation the water evaporates, thus cooling the cutting tool; the oil is deposited on the nascent met al surface, thereby preventing oxidation and serving as a lubricant [Groves, 1978].

Similar phenomena as the ones present in the milling process are found when rolling aluminum or steel down to sheet or thin foil, but in this case, the environmental temperatures are much higher and processes which occur during the rolling are far from being completely understood. It is believed that the stability of the cutting-fluid emulsion used in this case is critical, but as the met al surface may be as hot as 800 or 1000°C, it is clear that the evaporation of the aqueous phase must be extremely rapid, even though it may only be in contact with the met al surfaces for only a few milliseconds [Groves, 1978].

Finally, it is worthwhile to remark that the cutting oils themselves are made up by self-emulsification of oil concentrates with water in large tanks and pumped to the machinery, being recirculated after crude filtration if necessary.

1.5.7 Enhanced Oil Recovery

With the current technology involved in the primary oil recovery and flooding of oil wells (secondary oil recovery), only about 30 % w/w of the original petroleum in place is recovered from reservoirs [Baviere, 1997; Pillai, 1999; Rivas, 1997; Taber, 1981]. Much of this unrecovered oil remains as globules or drops trapped by capillary and viscous forces in the small pores of the sandstone rock, the remainder of the pore space being filled with water. This oil entrapment is accounted for by the capillary number, which normally has values of 10^{-6} after the secondary oil recovery. The capillary number is given by

$$\text{Capillary number}, \quad Nc = \frac{u\mu}{\phi\gamma} \tag{1-2}$$

where ϕ = porosity of the rock reservoir, γ = interfacial tension of the petroleum-water system (or surface tension when air is the second fluid in the well), μ = dynamic viscosity of the liquid used to remove the petroleum globules, and u = Darcy velocity of fluid in porous media.

To produce more oil from the well, a technology known as tertiary enhanced oil recovery (EOR) has been developed, which consists of several techniques. One of these techniques is the surfactant-polymer flooding which aims to increase the capillary number to 10^{-3} generally by lowering the interfacial tension (i.e., lowering the capillary forces), since reduction of the capillary forces by injection of suitable surfactant solutions

provides a way of lowering the interfacial tension sufficiently to allow economically viable recovery [Baviere, 1997; Groves, 1978; Pillai, 1999; Rivas, 1997; Taber, 1981].

In addition to the lowering of the capillary number, spontaneous emulsification can help to increase the rate of oil recovery by washing off the oil from the porous rock in the wells [Egbogah, 1985] when the surfactant partitions from the aqueous phase into the oil phase, spontaneous emulsification occurs and this mechanism leads to greater oil recovery. Displacement tests with spontaneously emulsifying systems showed that residual oil left behind by a conventional waterflood was mobilized in a range of capillary numbers much less than which applies to low-tension waterfloods.

It is important to mention that another mechanism that improves the surfactant-polymer flooding occurs when the surfactant partitions from the aqueous to the oil phase, promoting the increase of the volume of the residual oil drops. Since surfactants present in the oil phase tend to solubilize water, the volume of the residual oil drops is increased, consequently improving oil recovery by this mechanism [Shah, 1985].

Finally, it has been shown that the synergistic effect of combining small amounts of surfactant, normally less than 0.5 % w/w, together with an alkaline additive can produce ultralow interfacial tension against an acidic crude oil, improving oil recovery and promoting spontaneous emulsification [Campbell, 1981; Li, 2000; Rivas, 1997]. It is still unknown, however, whether transient (initial) interfacial tension or equilibrium interfacial tension are more important in improving oil recovery. What is known is that oil recovery is higher with the combination of surfactant and alkali than with either taken alone [Rivas, 1997; Rudin, 1994].

1.5.8 Formation of Nano-emulsions and Nano-particles

A substance made of nano-particles has several important characteristics. First of all, it has an enormous surface area (for example, a kilogram of such substance could have a surface area equivalent to approximately 3-4 football fields), which makes such substance suitable for important industrial applications like insulators for the semiconductor industry (such as SiO_2), and bases for poison absorbents, catalysis, paints, etc.). Second, the small size of the particles allows the substance to actively interact with the light, making it suitable for the fabrication of sun blocks. Finally, related to the present work, spontaneous emulsification has been found to have a major role in the production of nano-particles; role that can be conveniently divided into the three stages (1) emulsification, (2) droplet growth by coalescence, and (3) droplet gelation.

The following is an example of an industrial application of the production of nano-particles by means of a spontaneous emulsification. Minehan and Messing [1992] present a study on the production of the SiO_2 insulator from the common precursor tetraethoxysilane (TEOS).

First of all, Minehan and Messing [1992] use TEOS, water and ethanol to obtain the SiO_2. They report that emulsification at the water-alkoxide solution interface forms alkoxide-rich droplets in the water phase. This stage of particle formation depends on the ternary phase equilibrium among partially hydrolyzed tetraethoxysilane (TEOS), water and ethanol and the interfacial tensions between the liquids. The droplets rise because of the lower density of the silicate-alcohol solution. Droplet growth may occur during this stage by coalescence and therefore, can be influenced by the interfacial tensions between the liquids plus the initial droplet size and the rate of silicate gelation in the droplet. Particle size can be controlled during this stage by the rate of silicate gelation and thus by

the degree of silicate hydrolysis, the presence of water and the concentration and type of catalyst.

Two-step hydrolysis of TEOS yields a solution having the required molecular chemistry for the formation of submicron particles by the spontaneous emulsification process, as it has an enlarged immiscibility range when mixed with ethanol and water. Furthermore, the partially hydrolyzed silicate solution, as produced by two-step hydrolysis, consists of molecular species that lower the interfacial energies in the emulsion and thus the degree of droplet growth by free-energy driven coalescence. These silicates also can be rapidly gelled thus providing an important mechanism for limiting droplet coalescence. Depending on the molecular chemistry of the hydrolyzed TEOS, hollow, uniformly filled or collapsed spheres ranging in size from less than 0.1 μm to as large as 2.0 μm in diameter can be produced by this method.

To explain the spontaneous emulsification observed in this process, Minehan and Messing [1992] make reference to the diffusion and stranding mechanism that suggests that droplets form by a nucleation and a growth process from localized super-saturation near the interfacial region. In this case the, out-diffusion of ethanol from the silicate solution into the surrounding water results in silicate super-saturation. Emulsification is induced when the local composition crosses the two-phase boundary. The energy provided for mixing during ethanol diffusion is proportional to the difference between the change in free energy of unmixed ethanol and the partially hydrolyzed TEOS solution and the change in free energy of mixing water and ethanol.

1.5.9 Asphalt Emulsions: Bitumen Emulsion

According to Green [1998], bitumen emulsions represent a particular class of o/w emulsions in which the oil phase has a relatively high viscosity. These emulsions are

normally produced by dispersing hot bitumen in water containing a surfactant by using a colloid mill. The size of the droplets produced depends on a number of variables including bitumen viscosity, rotor-stator gap, rotor speed and the physicochemical conditions of the system. Nevertheless, most of the bitumen emulsion droplet distributions range between 1 to 20 μm. When the bitumen emulsions are used in their final application they "break" due to (1) water evaporation or (2) water-bitumen separation due to the chemical nature of the surface to which the emulsion was applied. It is important to stress the fact that the primary object of emulsifying the bitumen is to obtain a low viscosity product which can be used without the heating that is normally required for non-emulsified bitumens.

Bitumen emulsion formation could involve the reaction of the surfactant with a basic material such as sodium hydroxide ($RCOOH + NaOH \leftrightarrows RCOO^- + Na^+ + H_2O$) or the reaction with an acidic species such as hydrochloric acid ($RNH_2 + HCl \leftrightarrows RNH_3^+ + Cl^-$) (In both cases, R is a hydrocarbon chain).

Green [1998] indicates that the classification of bitumen emulsions, the British Standard specification for emulsions is BS 434: Part 1, 83. This classification specifies three categories (1) chemical type (A, anionic; K, cationic), (2) rate of break (1, rapid; 2, medium; 3, stable/slow; 4, slow), and (3) bitumen content expressed as a percentage of the total. Thus, for example K1 70 is a cationic, rapid breaking emulsion with nominally 70 % v/v bitumen, whereas A2 57 is an anionic, medium setting emulsion containing nominally 57 % v/v bitumen. (The bitumen content usually lies between 30 and 70 % v/v depending on the application for the emulsion).

The key requirements for bitumen emulsions are viscosity, stability, and rate of break. Furthermore, the viscosity, which determines the ease of handling, is influenced by the bitumen content, emulsifier loading, drop size distribution and temperature. However, the effect of those variables on the viscosity of the bitumen-in-water emulsion for bitumen contents up to approximately 60 % v/v is small. Nevertheless, an additional 5 % v/v in bitumen content has a significant effect on the viscosity; furthermore, if it is increased beyond 75 % v/v, there is a significant chance of not only an emulsion inversion, but also of a huge increment in the system viscosity (i.e., the system becomes "solid").

There is a critical balance between stability and rate of break of a bitumen emulsion in order to ensure its optimum performance. The emulsion should be sufficiently stable for storage and transportation purposes such that it does not drain or break, but it should readily break in use. (The rate of break of an emulsion dictates its end use. Thus, Green [1998] explains that emulsions used in surface dressing need to have a rapid rate of break so that there is a quick build up in bond strength between the aggregate and the binder. Consequently, K1 emulsions are used for this application. On the other hand, emulsions used for slurry seals and similar mixtures need a much lower rate of break so that the aggregate and the binder become intimately mixed; K3 emulsions are used for this application).

Finally, Green [1998] explains that the breaking of a cationic emulsion is usually initiated by a chemical reaction between the positively charged emulsion and the negatively charged aggregate. This type of reaction is much less likely to occur with anionic emulsions where the breaking process is governed almost entirely by the

evaporation of water. The absence of any chemical initiation of the breaking process means that anionic emulsions can be very sensitive to climatic conditions.

1.6 Spontaneity of Emulsification

Spontaneity for emulsification has not been well defined. Whereas in some references it is considered as the time to reach "the equilibrium conditions" at which the average drop size remain stable (indirectly, the rate of emulsion formation), in others it is qualitatively referred to as both the amount of emulsion formed spontaneously and its rate of formation [Groves, 1974].

A spontaneity test used widely in the industry is the Collaborative Pesticide Analytical Committee of Europe test (CPAC test), which defines the spontaneity as the ease of formation in qualitative terms as good, moderate, and bad. A 1 ml bulb pipette is supported vertically with the tip about 4 cm above the surface of water at the 100 ml graduation mark in a 100 ml measuring cylinder [Becher, 1983]. The oil content in the bulb is allowed to fall freely into the water and the ease of emulsion formation is expressed visually as good, moderate or bad. This method presents serious disadvantages such as (a) the most of the oils are lighter than water, and (b) the rate at which the oil will move depend strongly on the difference in density. However, it has been used amply in spite of its poor inter-laboratory reproducibility, because of its ease of application and because it does not require the use of sophisticated instrumentation [Becher, 1983].

Modern methods for measuring spontaneity are based on light scattering. Some of these methods report the time to reach a constant value in the average drop size as an indicative parameter of the spontaneity. The average drop size of a system that undergoes self-emulsification is monitored along time until it reaches a constant average drop size value. In the emulsion formation process, the mean particle size decreases at

the same time as the total number of particles increases. These processes continue until "the equilibrium conditions" between disruption and coalescence processes are reached. At this point, the particle size distribution and, possibly, the overall turbidity of the system will remain almost constant. The spontaneity will be studied as both the time to reach "the equilibrium conditions" at which the average drop size does not change, and the amount of emulsion formed spontaneously.

According to Groves and Mustafa [1974], by injecting a fixed volume of the oil into a flowing stream of water, and taking measurements downstream of the mixing point it is possible that information on the time needed to reach the equilibrium point might be obtained (i.e., the degree of "spontaneity" expressed as a time). Groves and Mustafa [1974] made a comparative analysis of their method with the CPAC test, and found that there is a close correlation between the two of them. (Their results are shown in Table 1-1).

Inspection of Table 1-1 shows that, although the constitution of the self-emulsifiable oil appears to affect the degree of spontaneity, there is also an approximate correlation with the results obtained from the qualitative CPAC test. For example, systems which take 7 s or more to come to equilibrium appear to be classified as having "bad" spontaneity whereas those emulsifying in less than 6 s are described as "good" [Groves, 1974].

Table 1-1. Qualitative spontaneity and time to reach equilibrium for a number of PNE-PFE-n-hexane systems at 25°C. Notice that there is a very good correlation between the results for the time to reach equilibrium and the qualitative information given by the CPAC test (with the exception of only three points that may have been wrong due to experimental limitations).

Concentration (% w/w)			CPAC test Result	Time [s] to reach equilibrium
PNE	PFE	n-Hexane		
15	15	70	g	5.66
12.5	12.5	75	g	5.66
10	10	80	g	5.9
25	25	50	b	6.37
7.5	7.5	85	m	6.37
22.5	22.5	55	m	6.5
17.5	17.5	65	m	6.5
5	5	90	m	6.5
20	20	60	m	6.8
2	8	90	b	7.4
8	2	90	b	7.6
30	30	40	b	7.7
35	35	30	b	7.85
18	2	80	b	8.4
2	18	80	b	8.5
3	27	70	m	9.5
27	13	60	m	9.6
36	4	60	b	10.2
4	36	60	b	10.2
45	5	50	b	10.8
5	45	50	b	10.8
54	6	40	b	11.3
6	54	40	b	11.4
63	7	30	b	11.8
7	63	30	b	12

(Adapted from Groves and Mustafa [1974]).

CHAPTER 2

MATERIALS, INSTRUMENTS AND METHODS

2.1 Materials

Brij30, Makon 4, Makon12, dioctyl sodium sulfosuccinate (AOT), Tween85, Brij35, sodium dodecyl sulfate (SDS), orange OT (an oil soluble dye), green Bromocresol (a water soluble dye) and hydrochloric acid were acquired from Sigma-Aldrich Co. In addition, Linear alkyl oils (i.e., C_8-C_{16}), mineral oil, sec-butanol, n-amyl alcohol, sodium chloride, aluminum chloride, phenol, ethyl butyrate, ethyl oleate, dodecyl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, hexadecyl trimethyl piridinium chloride, oleic acid, ammonium chloride and ammonium hydroxide were purchased from Fisher Scientific. Deionized distilled water was obtained from a Milli-Q-Plus water filtration system. Polyester fabric was obtained from Walmart.

2.2 Instruments

2.2.1 Balance

A balance (Sartorius, model BP211D) with 5 figures of precision was used to weight some of the substances used to prepare mixtures and solutions studied in this research. The balance was also required to weight the stain applied on polyester fabrics pieces (see Chapter 6).

2.2.2 Drop Counter Sizer

The drop size distribution and specific interfacial area experiments were carried out in a laser diffraction particle size analyzer (Coulter Counter Sizer LS 230).

2.2.3 Videos and Photographs

The videos and photographs that provided the optical evidence of the spontaneity of spontaneous emulsification and spontaneous detergency phenomena were taken by means of an Enhanced Videomicroscope (Olympus Model BX60; software Spot Advanced). The experiments in the microscope were also useful to explain the spontaneous emulsification mechanisms.

2.2.4 Conductivity-Temperature Meter

The phase inversion temperature (PIT) of the Brij30-hexadecane-brine systems was determined by monitoring the temperature simultaneously with the conductivity by mean of an Oakton conductivity-temperature meter. This device was also use to measure the temperature of other systems.

2.2.5 pH-Temperature Meter

The pH of the systems containing oleic acid, ammonium chloride and ammonium hydroxide and hydrochloric acid were measured by means of a pH-temperature meter.

2.2.6 UV-visible Spectrometer

In the detergency experiments, the mineral-oil/orange-OT system concentrations in water were determined by means of a Hewlett Packard 8453 UV-visible spectrometer. This instrument was also used to monitor the concentration of green Bromocresol and phenol in water for water purification experiments.

2.3 SYSTEMS

2.3.1 Spontaneity of the Emulsification Process

To validate the method to quantitatively determine the spontaneity of the emulsification process and to rank the effect of oil chain length on the spontaneity of the

emulsification process some Brij30/linear-alkyl-oils (i.e., C_8 to C_{16}) solutions were prepared at surfactant-to-oil ratio of 20/80 weight by weight (w/w) and injected into the counter sizer chamber which was kept full of water.

In a similar way, to study the effect of the pH and the ionic strength on the spontaneity of the emulsification of oleic-acid/hexadecane solutions at surfactant-to-oil ratio 20/80 w/w and, ammonium-hydroxide, ammonium-chloride, and sodium-chloride solutions at 5M were prepared. The effect of surfactant concentration on the drop size distribution and on the specific interfacial area was also studied. Here, $C_{12}E_4$/decane solutions at 0.02, 0.5, 2.5, 5, 10, 15, and 20 % w/w were prepared. Later, samples of these solutions were injected into the Coulter sizer chamber to control the physicochemical conditions of the water contacting the oil phase.

2.3.2 Liquid Crystal Instability

Solutions of Brij30/hexadecane were prepared at different surfactant-to-oil ratios (5/95, 10/90, 15/85, 18/82, 20/80, 26/74 and 30/70 w/w) in order to determine the mechanism for nano-emulsion formation when Brij30/hexadecane/water system are brought in contact with water. From these solutions, others systems were prepared by adding different amount of water (i.e., sweeping the water concentration from 0 to about 30 % w/w) to them. These systems were then used to study the effect of the temperature, and the surfactant-to-oil ratio, and initial water concentration on the drop size distribution and on the specific interfacial area as well to verify the spontaneous nano-drop formation under a microscope. In addition, others concentrations were explored to study the phase behavior and to build the schematic of the phase diagram for the Brij30/hexadecane/water system.

2.3.3 Diffusion and Stranding, Interfacial Turbulence, Negative Interfacial Tension, and Rayleigh Instability

Solutions of Brij30/hexadecane, aerosol-OT/hexadecane, and Brij30/aerosol-OT/hexadecane were prepared to study the effect of surfactant, surfactant-to-surfactant ratio and surfactant concentration on the spontaneous emulsification mechanism.

2.3.4 Detergency

Solutions of mineral-oil/orange-OT at 0.5 % w/w of orange OT, as well as solutions of Brij30/mineral-oil/orange-OT, Brij30/hexadecane, Brij30/water, and SDS/water were prepared at different surfactant concentrations ranging from 0 to 500mM. These systems were then used to study the effect of the surfactant, surfactant concentration, and the detergency protocol on detergency performance for the removal of mineral oil from a polyester fabric. In order to analyze the amount of oil removed from the polyester fabric by a HP 8453 UV-visible spectrometer, the analyte must first be dissolved to make it uniformly distributed and transparent. A SDS/n-amyl-alcohol aqueous solution at 2:1 volume/volume (v/v) ratio was used to dissolve oil the dispersed in water.

2.3.5 Water Purification

To study the removal of green Bromocresol and phenol from water by means of microemulsions the following systems were prepared stock solutions of (a) green Bromocresol at 1000 ppm, (b) phenol at 30 and 62 ppm, and (c) microemulsions systems according to the formulas listed in the Tables 2-1, 2-2, 2-3, 2-4, and 2-5. All the values in these tables are volume in milliliters (mL). Where 2L means a two phase system (an o/w microemulsion in the bottom in equilibrium with an oil phase in the top), 2U means a two phase system (an aqueous phase in the bottom and a w/o microemulsion in the top),

and 3 means a three- phase system (an aqueous phase in the bottom in equilibrium with a bicontinuous microemulsion in the middle and an oil phase in the top).

Table 2-1.   Microemulsion system containing SDS/C_{12}-oi, n-amylalcoho, and brine.

Test tube	Water	Brine	SDS	C_{12} oil	Amyl	Phase behavior
1	2	1	2	5	1	2L
2	1.8	1.2	2	5	1	3
3	1.6	1.4	2	5	1	3
4	1.4	1.6	2	5	1	3
5	1.2	1.8	2	5	1	2U

Table 2-2.   Microemulsion system containing C_{12}TAC, C_{12}-oil, n-amyl-alcohol, and brine.

Tubes	Water	Brine	C_{12}TAC	C_{12}	Amyl	Phase behavior
1	2.6	0.4	2	5	1	2L
2	2.4	0.6	2	5	1	3
3	2.2	0.8	2	5	1	3
4	2	1	2	5	1	3
5	1.8	1.2	2	5	1	3
6	1.6	1.6	2	5	1	3
7	1.4	1.4	2	5	1	2U

Table 2-3.   Microemulsion system containing Makon4, Makon12, C_{12}-oil, n-amyl-alcohol, and brine.

tubes	W	Makon12	Makon4	C_{12}	Amyl alcohol	Phase behavior
1	5.00	0.00	2.00	3.00	1	2L
2	4.85	0.15	1.85	3.15	1	3
3	4.80	0.20	1.80	3.20	1	2U

Table 2-4.   Microemulsion system containing SDS, ethyl-butyrate-oil, n-amyl-alcohol, and brine.

tubes	W	B	SDS	oil	Amyl	Phase behavior
1	1.4	1.6	2	5	1	2L
2	1.3	1.7	2	5	1	3
3	1.2	1.8	2	5	1	3
4	1.1	1.9	2	5	1	3
5	1.0	2.0	2	5	1	2U

For method 1, the aqueous phase (i.e., the surfactant, the water and the brine solutions) for the microemulsion were prepare from stock solutions of phenol and green Bromocresol at 62, and at 1000 ppm, respectively. The surfactant solutions have concentration of 0.35 M.

2.4 Methods

2.4.1 Determination of Droplet Size and Increase in Specific Interfacial Area (SIAT)

Samples of 10 μL of the prepared solution were added with a micropipet into the main chamber of the Coulter Counter Sizer, which was gently stirred at 480 rpm throughout the entire process. The stirring speed was sufficient to keep the emulsion well stirred. The chamber was kept filled to its maximum capacity of 125 mL with ultrapure water. After 90 s of operation and for certain time intervals set by the operator, the instrument reports statistical information, such as the specific interfacial area (S), drop size distribution and mean drop radius (R). All this statistical analysis is given by the Beckman Coulter software with the exception of the initial specific interfacial area (S_0), which nevertheless can be calculated as the area of a sphere with the initial radius $R_0 = 0.13$ cm. The calculation is performed according to the formula

$$S_0 = 4 * \pi * R_0^2 / (4/3) * \pi * R_0^3 \qquad (2-1)$$

where R_0 is the radius of the initial drop considering it as an sphere volume 10 μL. For this experimental setup, $S_0 = 23.08$ cm^2/mL, which represents the initial area per unit volume of dispersed phase.

The experimental procedure was repeated for different samples in order to thoroughly characterize the change in drop size and the increase of the interfacial area with respect to time.

For the systems that required temperature control it was achieved by means of a large tempered water reservoir which feeds water to the Coulter chamber at the desired temperature, depending on the specific case; on the other hand, the samples were kept on the inside of a tempered bath for several minutes to assure that they reach the working temperature.

For systems where the pH and the salinity were the factors to control, volumes of aqueous solution of NaCl, NH$_4$OH, and NH$_4$Cl at 5M were added to meet the condition specified for any particular experiment.

2.4.2 Phase Behavior

The phase behavior was analyzed at room temperature by two different techniques (1) dispersability in water, and (2) cross-polarized light. The dispersability in water technique was used for fairly clear phases. It consists of placing a drop of any of the clear-liquid phases of the prepared Brij30/hexadecane/water systems on top of water and observing the spreading process. If the system breaks into macroscopic oil droplets then it means that the phase is oil with probably low surfactant concentration; if the system emulsifies when in contact with water it is considered in this paper as a water-in-oil (w/o) microemulsion; furthermore, if the phase disperses very well when in contact with water it will be considered as an oil-in-water (o/w) microemulsion or probably a sponge phase microemulsion. The cross-polarized light lens technique was used to identify the existence of the lamellar liquid crystal phase, L$_\alpha$, which always shows birefringence, and the sponge phase, L$_3$, which is flow birefringent.

2.4.3 Phase Diagram

The main boundaries of the phase diagram of the Brij30/hexadecane/water system were determined by observing their phase transition behavior a room temperature when

(1) adding water to various surfactant/oil solutions at different ratios (from 5/95 to 100/0 w/w); and (2) adding surfactant to oil/water mixtures at different ratios ranging from 0/100 to 95/5. The phase transition behavior was studied by analyzing the characteristic changes in (viscosity (qualitatively)), birefringence through cross-polarized lens, cross-polarized microscopy to see the presence of Maltese crosses characteristic of lamellar liquid crystal phase and phase behavior properly, for systems whose phases separate fast.

2.4.4 Phase Inversion Temperature (PIT)

Phase inversion temperatures were determined by monitoring the conductivity of several (Brij30/hexadecane)/water (at 0.02 NaCl %weight /volume (%w/v)) systems at 50/50 v/v at different surfactant-to-oil ratios by means of a conductimeter. When water is the external phase conductivity is high, which shift towards low conductivity values when oil is the external phase. In this case, the PIT was taken as the temperature where there is a steep decrease in conductivity.

2.4.5 Spontaneity

The spontaneity of the emulsification process was studied by means of an enhanced video microscope. A drop of the prepared systems was placed in a Petri dish and water was added gently and the emulsification monitored by a video camera to corroborate that the Brij30/linear-alkyl-oil system thoroughly emulsify with or without little aid of external energy.

2.4.6 Diffusion and Stranding, Interfacial Turbulence, Negative Interfacial Tension, and Rayleigh Instability

The spontaneous emulsification process was monitored by means of a video camera set in an enhanced video microscope. Then, photographs of the interfaces undergoing different instabilities were taken to show the main characteristics of some of

the different mechanisms (i.e., the drop sizes that they produce and the kind of instabilities that give them the name).

2.4.7 Detergency Experiments

Four detergency protocols were assayed (1) Brij30 is mixed with mineral-oil/orange-OT solutions and then the mixture is applied to a circular pieces of polyester fabric (the substrate) of a diameter of approximately 1 inch, and left to rest for 4 hours; (2) a mineral-oil/orange-OT solution is applied to polyester fabric pieces and left to rest for approximately 4 hours, then 70μL of a Brij30/hexadecane solution is added to the stain and left to spread through the fabric for 4 minutes; (3) amineral-oil/orange-OT solution is applied to the polyester fabric pieces and left to rest for approximately 4 hours and then 70μL of a Brij30/water or SDS/water systems are added to the stain and left to spread through the fabric for 4 minutes; and (4) Mineral-oil/orange-OT solutions are applied to the polyester fabric pieces and left to rest for approximately 4 hours, and then 4 mL of water is gently added to the fabric in a vial follow by the addition of 70 μL of Brij30/water solution. In the case of protocols 1, 2, and 3, 4 mL of water are gently added to the stained fabric in a vial. The piece of fabric with the remaining oil is removed from the vial after 0.5, 1, 5, 10, and 20 minutes, thus, leaving in the vial a heterogeneous oil-water mixture. The leftover heterogeneous mixture must be first dissolved before subjecting it to UV-visible spectrometry. To solubilize the leftover mixtures, 10 mL of an SDS/water/n-amyl-alcohol solution at 2:1:1 volume ratio is added to each of them.

2.4.8 Water Purification

In order to remove green Bromocresol and phenol from water, two methods based on the liquid-liquid extraction process were used. In the first one, method 1, a water

source containing hazardous molecules was formulated with surfactant/co-surfactant/oil/brine systems to produced systems of two or three phases. These formulated systems are then thoroughly mixed forming an o/w emulsion that keep the water and the oil in close-contact along a huge interfacial area. This large interfacial area facilitates the mass transfer from one phase to the others and vice versa. The mass transfer process among the phases and the interface also takes place. Few minutes after the mixing process is stopped, the emulsion separates into its constituting phases. The bottom portion is taken and analyzed by means of a HP 8453 UV-visible spectrometer. In the second one, method 2, water containing hazardous components is mixed with a bicontinuous or a w/o microemulsion, thus, inducing the formation of an o/w nano-emulsion which provide a large interfacial area and a huge number of droplets. These two factors, the huge area and the large numbers of droplets are suitable conditions to enhance the liquid-liquid mass transfer. Approximately 1 hour after the phases have been in contact, the emulsion is destabilized by adding aluminum salt and the resulting dispersion is filtrated by means of a 200 nm mesh filter. The filtrated water is then analyzed by means of a HP8453 UV-visible spectrometer.

The precipitation of the microemulsion containing cationic surfactants was achieved by adding an aqueous solution of SDS at surfactant to co-surfactant ratio around 1. Then an aqueous solution of aluminum chloride was added to precipitate the excess of SDS.

CHAPTER 3
A NEW METHOD TO QUANTITATIVELY DETERMINE THE SPONTANEITY OF THE EMULSIFICATION PROCESS

3.1 Introduction

Spontaneous emulsification is a phenomenon that occurs when two immiscible liquids are brought in contact with each other and the mixture emulsifies without the aid of any external thermal or mechanical energy source. Depending on the liquids involved, the presence of appropriate surfactants, pH, or other imposed potentials, it may take from a few minutes to several days for completion of the spontaneous emulsification process [Miller, 1988].

In practice, when two immiscible liquid phases undergo spontaneous emulsification, one only observes the rapid formation of cloudy dispersions; hence, it is difficult to measure the kinetics of spontaneous emulsification. Nevertheless, recent advances in video imaging, laser diffraction, and light scattering techniques for size distribution of droplets have made it possible to measure the rate of spontaneous emulsification. However, the technique currently used in industry to measure the spontaneity of an emulsification process is known as the Collaborative Pesticide Analytical Committee of Europe test, commonly referred to as the CPAC test [Groves, 1974; Becher, 1983].

Spontaneity is one of the most important characteristics of the spontaneous emulsification process. Nevertheless, there was not a reliable method to quantify it. In this chapter, the heart of this dissertation is presented: A new method to quantitatively

determine the spontaneity of the emulsification process, the so-called Specific Interfacial Area Test (SIAT). This method is a powerful tool that is simple to use and is meaningful (i.e., quantify the emulsification process at its most essential characteristic, the total interfacial area as a function of the time) in determining the rate and the total increase in interfacial area due to emulsification. We hope that in the near future this method becomes a common tool among researchers that study the emulsification process taking advantages of its unique characteristics (meaningfulness and simplicity). In the next chapter it will be shown that this method can be used to rank the different factors affecting the spontaneous emulsification phenomenon, to diagnose the occurrence of different mechanisms, to suggest the best way to prepare emulsions with different droplets size distribution and to suggest system that would enhance the potential applications of this phenomenon.

3.2 Spontaneity Tests

In this section the most important tests designed to measure the spontaneity of the emulsification process will be described.

3.2.1 CPAC Test

In this technique, a 1 mL bulb pipette is vertically supported with the tip about 4 cm above the surface of water at the 100 mL graduation mark in a 100 mL graduated cylinder [Groves, 1974; Becher, 1983]. The oil content in the bulb is allowed to fall freely into the water, and the ease of emulsion formation is visually evaluated and expressed in a qualitative fashion as good, moderate, or bad. This method presents serious disadvantages such as the following: (a) the data obtained cannot be meaningfully compared to data obtained in other laboratories, since this technique relies on visual appreciation; (b) most oils are lighter than water, that is, only a few oil layers will be in

contact with fresh water, thus slowing down the emulsification rate; and (c) the rate at which the oil will disperse down into the water phase strongly depends on the difference in density between the oil and water. However, the CPAC test has been widely used despite its poor interlaboratory reproducibility, mainly because of the ease of its application and because it does not require the use of sophisticated instrumentation [Groves, 1974; Becher, 1983].

3.2.2 Turbidity Test

Groves and Mustafa [1974] suggest that the spontaneity for emulsification can be correlated with the time needed to reach the turbidity equilibrium value after injecting a fixed volume of oil into a flowing stream of water; that is, the degree of "spontaneity" is expressed as a characteristic time. This method reports the time required to reach a constant value of average drop size as an indicative parameter of emulsion spontaneity. The turbidity of a system that undergoes self-emulsification is monitored over time until it reaches a constant average value. In the emulsion formation process, the mean drop size decreases while the total number of drops increases. It was assumed by Groves and Mustafa [1974] that these processes continue until the equilibrium conditions between disruption and coalescence processes are reached. At this point, the particle size distribution, and possibly the overall turbidity of the system, will remain nearly constant. Therefore, emulsification spontaneity is characterized as the time required for reaching the equilibrium conditions where the average drop size does not change. This method has a major drawback; namely, that even though the time to reach equilibrium is a good approach to characterize of the kinetics of emulsification spontaneity, it nevertheless does not provide information on the extent of the emulsification process (i.e., the amount of interfacial area created). Finally, Groves and Mustafa [1974] made a comparative

analysis of their method with the CPAC test and found that there is a close correlation between the two techniques [1974].

3.2.3 Specific Interfacial Area Test (SIAT)

In the present work, it is proposed that the spontaneity of an emulsification process should account not only for the rate of emulsification but also for the volume fraction of the final internal phase as well as for the drop size distribution of the produced emulsion (or the total expanded interfacial area). The present work provides a simple approach to assess the spontaneity of some systems in a quantitative way. The proposed method assumes that emulsification is an energy-driven process which is directly related to the formation of the new interfacial area. The interfacial free energy increases as the interfacial area grows due to the breakage of drops into smaller droplets, and the dispersed volume remains constant. In the case of a spontaneous process, the required interfacial free energy is provided by the excess internal energy of the system upon mixing of the two liquids. Consequently, the spontaneity is directly related to the magnitude of the free energy of the system. The minimum energy (ΔG_{int}) required to create new interfacial area is then given by the integral of the interfacial tension (γ) with respect to the increase in interfacial area (dA), namely,

$$\Delta G_{int} = \int \gamma dA \tag{3-1}$$

with both being γ and A time-dependent parameters.

To test the proposed method, Brij30 was dissolved in several linear alkyl oils (specifically, C_8-C_{16}). The Brij30/linear-alkyl-oil/water systems were chosen because, according to Forgiarini et al. [2000, 20001] they show formation of nano-emulsions with low energy consumption, suggesting the possibility of the presence of a spontaneous

emulsification phenomenon. Lopez-Montilla [2002b] found that the spontaneous emulsification process that these systems undergo appears to follow several mechanisms. Figure 3-1 schematically represents the phase diagram of the Brij30/linear-alkyl-oil/water systems and the phase transition that takes place as the Brij30/oil system evolves from its initial concentration at point A to the final concentration at point E. Phase diagrams for the systems Brij30/decane/water have been made by Forgiarini et al. [2000, 2001] and we made the diagram for the Brij30/hexadecane/water system. The diagrams present striking similarities, and the assumption is made that the rest of the systems used in this work follow an analogous pattern. The dashed straight line connecting points A and E represents the spontaneous emulsification process protocol. Point A corresponds to the initial concentration, and point E is the final concentration reached when the spontaneous emulsification process is over.

3.3 Results and Discussion

The hypothesis furthered in this work is that one should be able to directly measure the spontaneity of the process by measuring the variations in specific interfacial area with time. The proposed method, sketched in Figure 3-2, consists of determining the two factors contributing to emulsification spontaneity, S (1) the spontaneity kinetic parameter (Ω), which is the initial rate of change of the specific interfacial area with time, and (2) the equilibrium parameter (Φ), which is the final specific interfacial area attained by the system and its value is not affected as the time progress.

This can be expressed as a vector.

$$S = \begin{pmatrix} \Omega \\ \Phi \end{pmatrix}$$

(3-2)

where S is the spontaneity vector. Note that

$$\Omega = \frac{dS}{dt} = \frac{1}{V}\frac{dA}{dt} \qquad\qquad (3\text{-}3)$$

and

$$\Phi = \underset{t\to\infty}{Lim}S(t) \qquad\qquad (3\text{-}4)$$

where t is time, A is the total interfacial area, V is the total volume of the dispersed

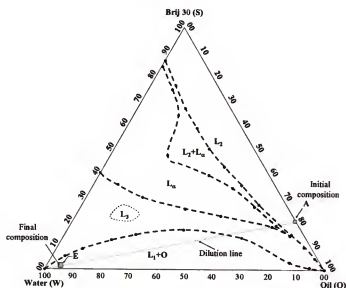phase, and S is the specific interfacial area defined as S = A/V.

Figure 3-1   Show the schematic of the pseudo ternary triangle phase diagram and the emulsification protocols follow in this study for the Brij30/hexadecane/water systems. This diagram shows the three components (surfactant, S; Oil, O; water, W) at any of the cornels of the triangle, different single phase (sponge, L_3; w/o microemulsion, L_2; and lamellar liquid crystal, L_α) and multiphase regions where some of the L_1, L_2, L_α, L_3, and O phases can co-exist. It also shows the dilution line, dashed lines on the phase diagram, connecting points A and E which represents the spontaneous emulsification protocols.

The schematic of the expected increase in specific interfacial area with time for

spontaneous emulsifying systems shown in Figure 3-2 has three zones, as follows: (1)

Spontaneous Emulsification Zone, here, the large drops massively split into droplets (i.e.,

the specific interfacial area increases quickly) due to the large initial amount of excess

internal energy available for this process. This region presents an almost linear behavior, whose slope defines the spontaneity kinetic parameter (Ω). (2) Emulsification Extinction Zone, at this point the spontaneous emulsification process rate slows down because the initial driving force decreases as the chemical potential of the surfactant in the various phases approaches an equilibrium condition. (3) Equilibrium Zone, this region corresponds to the final condition reached by the system, once the spontaneous emulsification process is over. This final value of the specific interfacial area represents the spontaneity equilibrium parameter (Φ).

Figure 3-2   Schematic of the expected change of specific interfacial area with time; this is directly related to the quantitative measurement of the spontaneity. Zone 1 corresponds to the spontaneity kinetic parameter (Ω), i.e., the slope of the straight line. Zone 2 corresponds to an intermediate region where the spontaneous emulsification process finishes due to energetic constraints. Zone 3 represents the equilibrium condition reached by the system once the spontaneous emulsification is over. This is directly related to the extension and completion of the emulsification process.

The schematic of the expected increase in specific interfacial area with time for spontaneous emulsifying systems shown in Figure 3-2 has three zones, as follows: (1) Spontaneous Emulsification Zone, here, the large drops massively split into droplets (i.e.,

the specific interfacial area increases quickly) due to the large initial amount of excess internal energy available for this process. This region presents an almost linear behavior, whose slope defines the spontaneity kinetic parameter (Ω). (2) Emulsification Extinction Zone, at this point the spontaneous emulsification process rate slows down because the initial driving force decreases as the chemical potential of the surfactant in the various phases approaches an equilibrium condition. (3) Equilibrium Zone, this region corresponds to the final condition reached by the system, once the spontaneous emulsification process is over. This final value of the specific interfacial area represents the spontaneity equilibrium parameter (Φ).
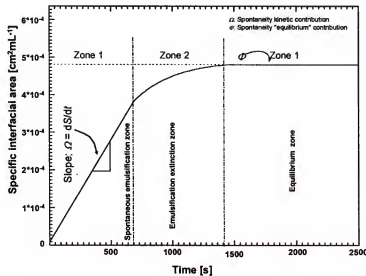
Figure 3-3a shows the differential drop size distributions of the Brij30/C_{12}/water system for three different times, starting at 90 s after the oil phase is brought in contact with water. A t initial time, three different modes are clearly distinguished (1) mode I, drops in the order of 100 μm, (2) mode II at 3 to 5 μm and (3) mode III occurring at 0.2-0.3 μm. It is proposed that mode II and mode III are generated as a consequence of the spontaneous emulsification process, while mode I is generated by mechanical forces present in the system due to the stirring. The large drops (mode I) disappear as they spontaneously emulsify with time.

Figure 3-3b illustrates the effect of the oil chain length on the volume-weighted droplet size distribution for three different Brij30/alkyl-oil/water systems at 90 s. Here, the oil chain length appears to have a strong effect on the drop size distribution changing the distribution from mono-modal to multimodal. For short chain length oils only one mode (i.e., mode II) is present; as the oil chain length increase two additional modes appear (i.e., mode I and mode III). The formation of drops with a mean diameter on the

order of 5 μm was a common occurrence among all the systems (mode II in Figure 3-3b). It is believed that mode II is a direct consequence of the spontaneous emulsification process since this is the only common feature among all the drop size distributions and considering that all these systems have been observed to spontaneously emulsify [Forgiarini, 2000; Forgiarini, 2001; Lopez-Montilla, 2002b]. Systems with longer oil chain lengths additionally present a mode around 0.2-0.3 μm (mode III) which cannot be formed by mechanical means unless a very large amount of energy is applied to the system. The generation of extremely small submicron-size droplets (mode III) provides additional evidence that spontaneous emulsification is taking place in these systems. The formation of these submicron droplets appears to be due to the formation and posterior destruction of liquid crystal structures [Lopez-Montilla, 2002a, Lopez-Montilla, 2002b] when water contacts the Brij30/oil systems (see dilution line crossing the liquid crystal zone in Figure 3-1). Liquid crystal structures exhibit ultralow interfacial tension to the water [De Gennes, 1982; Kellay, 1994] and they are destabilized as water penetrates into them and separates their lamellas which break into tiny drops according to a specific length scale [De Gennes, 1982; Kellay, 1994]. Thus, this explains the absence of mode III in the short chain length oil systems which do not have the tendency to form liquid crystal structures. These very small drops have a dramatic contribution to the increase of the specific interfacial area. Oils with long oil chain length present a third mode of drop size around 50-300 μm (mode I) that might correspond to drops of highly viscous systems due to the presence of the liquid crystal structures which later disintegrate into smaller drops as shown in Figure 3-3a.
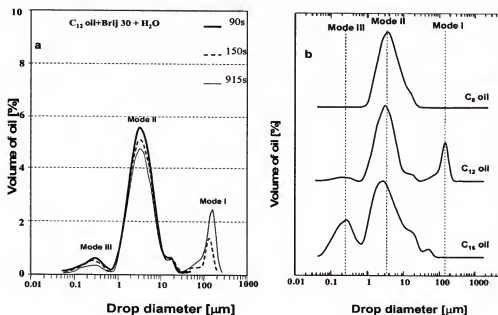
Figure 3-3. (a) Differential droplet size distributions of the Brij30/C_{12}/water system for three different times. The volume-weighted distribution indicates how much oil was emulsified with each particular drop size. (b) Effect of the oil chain length on the volume-weighted drop size distribution for various Brij30/alkyl-oil/water systems at 90 seconds. C_8 oil, C_{12} oil, and C_{16} oil refer to the Brij30/n-octane/water 20 % w/w surfactant, Brij30/n-dodecane/water 20 % w/w and Brij30/n-hexadecane/water systems 20 % w/w, respectively.

Furthermore, drop sizes corresponding to mode II (diameter = 3-5 μm) are in good agreement with experimental observations of the same systems made by Lopez-Montilla et al. [2002b] using enhanced videomicroscopy. They observed that the systems studied here present a strong interfacial instability and formation of a liquid crystal phase. They also note that when a drop of oil is brought in contact with water, the oil drop splits into droplets of difference sizes. We believe, based on these observations, that the formation of mode II in the distributions presented in Figure 3-3b is driven by a combination of low interfacial tension and interfacial instabilities such as interfacial turbulence. Figure 3-4 is a schematic representation of the spontaneous emulsification

mechanisms that I propose for the formation of mode II and mode III regarding the facts discussed above.

The effect of the oil chain length on the final specific interfacial area (Φ) and its rate of increase as a function of time (Ω) for different Brij30/alkyl-oil/water systems is presented in Figures 3-5 and 3-6. Figure 3-5 presents the trend of the expansion of the specific interfacial area as a function of time and is in good agreement with the expected spontaneity behavior outlined in Figure 3-2. Here, two intriguing observation can be point it out (1) the system containing C_{16} shows a much higher spontaneity than the rest of the systems and (2) in the C_{15} system the decay in the emulsification rate is slower which makes the interfacial area increase for longer time.
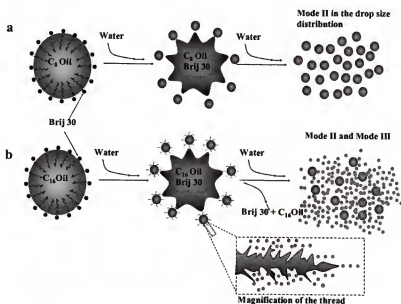

Figure 3-4. Schematic representation of the proposed spontaneous emulsification mechanisms for the system Brij30/alkyl-oil when brought in contact with water: (a) Brij30/n-octane 20 % w/w; (b) Brij30/n-hexadecane 20 % w/w.

Figures 3-6a and 3-6b respectively illustrate the initial slope, Ω, and the equilibrium values, Φ, of the interfacial area curves versus the oil chain length.

Originally, it was hypothesized that systems containing C_{12} would produce a lower water-oil interfacial tension than that of other oils since Brij30 ($C_{12}E_4$) and dodecane (C_{12}) would present oil chain length compatibility [Chan, 1981; Shah, 1980]. As a consequence of the expansion on interfacial area would be larger for the systems containing C_{12} oil than in the others cases. As one can see from Figures 3-6, the experimental results not only present the expected maximum for C_{12} but also show an unexpected large increase of the spontaneity kinetic parameter for long oil chain lengths (C_{15} and C_{16}). As before, the higher emulsification in the systems with longer oil chain length can be explained by the fact that an increase in the oil chain length increases the tendency for Brij30/oil systems to form liquid crystal when they are brought in contact with water; this liquid crystal structure that has been proved to emulsify the most [Lopez-Montilla, 2002b].
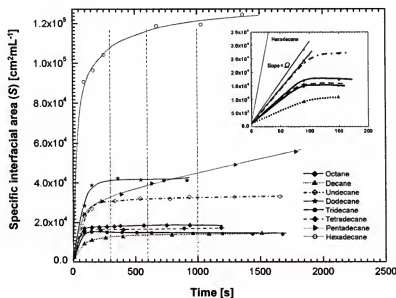

Figure 3-5. Experimental results for the change of the specific interfacial area with time for various Brij30/oil/water systems. The inset at the upper right corner is a magnification of the left bottom corner of this plot, and it is shown to clarify the fact that the slopes are calculated making the assumption that the emulsification process follows a straight line up to a time of 90 s.
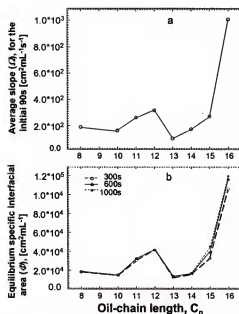
Figure 3-6. (a) Effect of oil chain length on the spontaneity kinetic parameter (Ω) of the emulsion process for the Brij30/oil/water system. (b) Effect of oil chain length on the spontaneity equilibrium parameter (Φ) of the emulsion process for the Brij30/oil/water system. Data were obtained from Figure 3-4.

3.4 Conclusions

The proposed method is an effective approach to quantitatively measure the spontaneity of the spontaneous emulsification process of the systems analyzed in the present work (see Figures 3-5 and 3-6).

The spontaneous emulsification process causes the volume-weighted drop size distribution to vary with time toward a distribution with lower droplet diameters (see Figure 3-3a). The oil chain length also has an important effect on the volume-weighted drop size distribution, which in turn dramatically affects the specific interfacial area expansion, that is, the spontaneity (see Figure 3-3b).

The spontaneous emulsification of the Brij30/linear-alkyl-oil systems put in contact with water produces a multimodal volume-weighted drop size distribution. Drops

corresponding to mode II and mode III (see Figure 3-3a and 3-3b) are produced by two different spontaneous emulsification mechanisms (see Figure 3-4). The formation of droplets corresponding to mode II (the only common mode of the drop size distributions for the different systems) is due to a combination of several spontaneous emulsification mechanisms regardless of the oil chain length (i.e., this mode is present in the distribution of any of the systems studied). On the other hand, presence of liquid crystal for longer chain length oils appears to be the responsible for mode (mode III).

Systems containing dodecane, pentadecane, and hexadecane turned out to be the systems with the highest kinetic and equilibrium parameters; therefore, these systems present the highest spontaneity among all the systems studied, that is, they emulsify more easily (see Figures 3-6a and 3-6b).

Finally, it is to be stressed that the "equilibrium" and the kinetic parameters of the spontaneity of the emulsification process for the systems studied yielded the same trends (see Figures 3-6a and 3-6b).

CHAPTER 4
RANKING OF FACTORS AFFECTING SPONTANEOUS EMULSIFICATION

4.1 Introduction

Traditionally, an emulsion has been defined as a system formed by two immiscible liquid one of them dispersed into the other in the form of droplets by a process called emulsification [Miller, 1988]. These systems have gained an important place in science as well as in technology mainly due to the unique combination of properties that these systems offer [Becher, 1983;Forgiarini, 2000; Forgiarini, 2001;Groves, 1978; Lopez-Montilla, 2002a; Miller, 1988; Ozawa, 1997; Pillai, 1999]. They have properties such as drop size distribution, large liquid-liquid interfacial area and the existence of at least two bulk phases with different polarities, hence, high solubilization capacity for both polar and non-polar solutes. However, controlling emulsion properties such as stability and drop size distribution is not always an easy task because they depend on many factors, among others, temperature, composition (component structures and component concentrations), and emulsification protocol. Furthermore, the droplet size distribution affects most of the other emulsion properties. Therefore, the factors affecting the emulsification process have been studied in relation to the factors that change the drop size and drop size distribution. In this respect, emulsion mean drop and emulsion drop size distribution have been very useful in evaluating the effect of different parameters on the emulsification and on emulsion properties. However, analyzing these two parameters to establish a relationship between them and the emulsion properties or the emulsification performance is not always straight forward.

As mention in chapter 3, a complementary and simpler parameter to evaluate the factors affecting the emulsification is the specific interfacial area. The main advantage of using the interfacial area as the parameter to assess the factors affecting the emulsion properties and the emulsification process performance lie on that it is much more sensitive than the drop size and it is easier to correlate with any emulsion property change than the drop size distribution since it is a number. Beside that, the specific interfacial area can be correlated with the interfacial Gibbs free energy. It is, however, important to stress the fact that the specific interfacial area would not fully substitute the mean drop size and the drop size distribution as a criterion to assess the factors affecting the emulsification process, but it would be a more sensitive complementary parameter able to sense small changes undetectable by the drop size distribution.

In this chapter, the effect of different variables such as surfactant concentration, surfactant to co-surfactant ratio, pH, salinity, etc., affecting two of the most important emulsion properties will be assessed (1) emulsion specific interfacial area and (2) the drop size distribution (note that this chapter is an extension of the chapter 3).

4.2 Results and Discussion

Surfactant concentration constitutes one of the most important parameters that affects the emulsion properties and the emulsification process performance. Figure 4-1 shows the effect of the effect of surfactant concentration on drop size distribution on the specific interfacial area produced when a $C_{12}E_4$/hexadecane solution drop is injected into the Coulter sizer chamber which is filled with water. In Figure 4-1a it is observed that at 20 % w/w of surfactant concentration the drop size distribution is a bimodal function with modes around 0.3 and 2 μm. As the surfactant concentration decreases, the distribution is

shifted towards the larger drop sizes. The probability of small-drop mode (0.3 μm) becomes smaller as the concentration decreases and it equals zero at 10 % w/w surfactant concentration. Furthermore, the probability of the mode located at 2 μm also decreases as the surfactant concentration decreases and it almost equals zero at concentrations of 0.5 % w/w or lower. For low concentration (2.5 % w/w or less) other mode appears, although, it changes towards higher drop sizes as the concentration decreases. Figure 4-1b illustrates a complementary way to monitor the emulsification process performance. This figure presents the interfacial vs. the surfactant concentration. As the surfactant concentration change from 0.02 to 20 % w/w, the interfacial area change to produce three different zones (slops) (1) pre-diffusion and stranding mechanism zone. In this zone, the specific interfacial area increase linearly with the surfactant concentration. Simultaneously from Figure 4-1a, one can see that the probability of the mode located at 2 μm increases as the surfactant concentration increases and vice versa. Then, a second zone, in which the specific interfacial area reaches a plateau, appears. From Figure 4-1a, the distributions curve around the mode 2 μm changes its shape but not very much. Finally, after the concentration exceeded 10 % w/w, a third zone appears (i.e., zone 3 where the liquid crystal zone instability mechanism takes place) (see chapters 3 and 5). Here, a steep increase on the specific interfacial area as the concentration increases is observed.

This surfactant is hydrophobic, hence, it does not have tendency to partition to the water although it partition to the oil-water interface. Nevertheless, as the surfactant concentration increases from zero to 10 % w/w the surfactant/oil solution is able to take more water (see Figure 3-1). This increase in the capability to take water of the

surfactant/oil solution with the increase in surfactant concentration makes higher the

probability that the oil strands forming oil drops of uniform sizes.
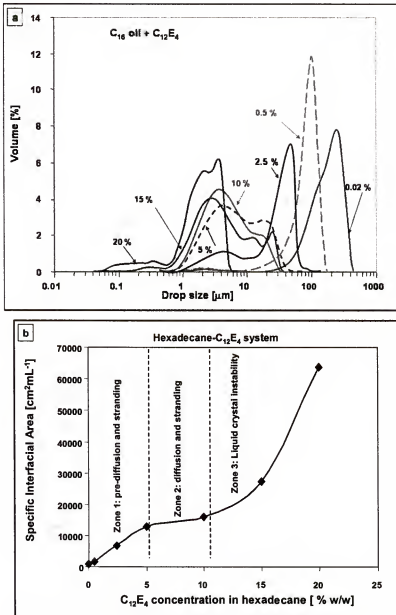
Figure 4-1. Volume weighted drop size distribution and specific interfacial area vs.
surfactant concentration of the emulsion formed when a drop of
$C_{12}E_4$/hexadecane solution drop at different $C_{12}E_4$ concentration (0.02, 0.5,
2.5, 5, 10, 15 and 20 % w/w) is injected into the Coulter sizer chamber
which is filled with water. Figure 4-1a presents the drop size distribution
and Figure 4-1b the expansion of the specific interfacial area vs. $C_{12}E_4$
concentration.

The diffusion and stranding mechanism takes place in zones 1 and 2. In zone1, as the surfactant concentration increases, the part of the system that would be emulsified by this mechanism increases, hence the mode probability as well as the interfacial area does increase. Meanwhile, in the zone2, the surfactant concentration is high enough to induce the whole system to emulsify under diffusion and stranding mechanism. This explains why the interfacial area does not increase when the surfactant concentration increases (i.e., in the range of surfactant concentration corresponding to the zone2, the whole system emulsifies under the same mechanism which can only produces certain drop sizes). At higher surfactant concentration (zone3), however, the system does not only have the possibility to undergo emulsification via diffusion and stranding but also a portion of it emulsifies under another mechanism. In chapter 3, it was suggested that submicron drops can be produced by liquid crystal instability and in chapter 5 detailed proof of this mechanism is addressed. It is also shown that this system emulsify under this liquid crystal mechanism occur in this system at Brij30 concentration over 15% w/w. It is also important to notice that the large-drop mode at low surfactant concentration (< 2.5 % w/w) and lower shifts as the surfactant concentration changes. This mode shift suggests that its occurrence is not a characteristic of the system but a consequence of the combination of the system properties and process performance.

In the remaining part of this chapter, I would like to show how useful this method can be rather than to find explanation for the molecular mechanism of the emulsification process or about the observed behaviors and trends. First, it is well known that the mixture of surfactants induces synergisms that enhance the performance of these molecules in their respective applications. In the case, the synergism from a surfactant

mixture we are trying to find the one that aims to enhance the emulsion stability, to have better control over the drop size distribution and especially to have a control on the interfacial area.

In the remaining part of this chapter, I would like to show how useful this method can be rather than to find explanation for the molecular mechanism of the emulsification process or about the observed behaviors and trends. First, it is well known that the mixture of surfactants induces synergisms that enhance the performance of these molecules in their respective applications. In the case, the synergism from a surfactant mixture we are trying to find the one that aims to enhance the emulsion stability, to have better control over the drop size distribution and especially to have a control on the interfacial area.

Figures 4-2 shows the effect of surfactant to co-surfactant ratio on the drop size distribution and on the specific interfacial area along time of the emulsion formed when a $AOT/C_{12}E_4$/decane solution drop is injected to the Coulter sizer chamber which is filled with water. The different AOT-to-$C_{12}E_4$ ratios used here were (5:0, 4:1, 3:2, 2:3, 1:4, 5). This figures show that these surfactant mixtures produce synergistic effect on the specific interfacial area and on the drop size distribution. Figure 4-2a illustrates the drop size distribution along time of the emulsion formed from the $AOT/C_{12}E_4$/decane system at AOT-to-$C_{12}E_4$ ratio 1:4. Here, it is observed that the distribution moderately change during the first 10.88 minutes, but after that, the distribution shifts towards drop size values much smaller. Meanwhile, Figure 4-3b shows the kinetic behavior of the expansion of the specific interfacial area for the $AOT/C_{12}E_4$ system at different AOT-to-$C_{12}E_4$ ratios. In this figure, it is observed that at the 4:1 and 1:4 AOT-to-$C_{12}E_4$ ratios, the

interfacial area expands slowly at the beginning and then it suddenly shift to much higher values. For the other ratios (except for $C_{12}E_4$), a similar trend is observed but at lower magnitude. This suggests that AOT is the component that induces the "jump" in the interfacial values but it is the combination of both surfactants that induces the synergism.
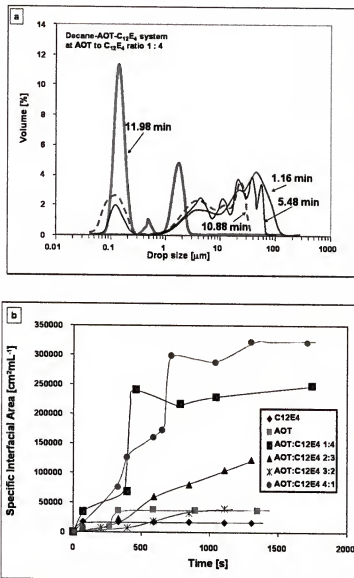
Figure 4-2. Volume weighted drop size distribution and specific interfacial area vs. surfactant concentration of the emulsion formed when a drop of $C_{12}E_4$/hexadecane solution drop at different $C_{12}E_4$ concentration (0.02, 0.5, 2.5, 5, 10, 15 and 20 % w/w) is injected into the Coulter sizer chamber which is filled with water. Figure 4-2a presents the drop size distribution and Figure 4-1b the expansion of the specific interfacial area along time.

In the next two chapters it will be shown that the drop size distribution is controlled by the spontaneous emulsification mechanisms. In this respect, it appears that the combination of both surfactants induces the occurrence of another spontaneous emulsification mechanism different than those undergo by the surfactants alone.

Enhanced oil recovery has become a very important technology that is used in several countries including the United States of America. In order to make this technology more profitable, petroleum companies are using as part of their formulations the naturally occurring surfactants in the crude oil. These surfactants are mainly carboxylic acids which can be and are activated by an alkali solution of sodium hydroxide. However, there are some questions that one has to answer in order to make the natural surfactants work for us. For instance, what are the better conditions (e.g., pH, alkali concentration and ionic strength) to produce the crude oil? In the Figures 4-3 and 4-4 I have partially addressed some of these questions. They show the combined effect of the pH and the alkali concentration, and the salinity, respectively, on the specific interfacial area of the emulsion formed when an oleic-acid/hexadecane solution drop is injected into the Coulter sizer chamber filled with aqueous solution containing NH_4OH and NH_4Cl and $NaCl$ at different concentrations. Here, we can see that the system present a maximum on the specific interfacial area at both alkali concentration. For the alkali solution at 100 mM the maximum is located between 8.34 and 9.14 units of pH for 100 mM whereas for the solution at 40 mM the maximum is located around 9 units of pH. It is well known that these systems emulsify by the interfacial turbulence mechanism [Rudin, 1994].
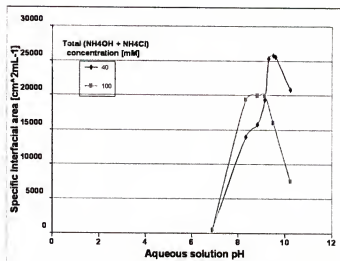
Figure 4-3. Shows the combined effect of the pH and the alkali concentration on the specific interfacial area of the emulsion formed when an oleic-acid/hexadecane solution drop is injected into the Coulter sizer chamber filled with aqueous solution containing NH_4OH and NH_4Cl and $NaCl$ at different concentrations.

In chapter 6, a correlation between the drop size and the emulsification mechanism will be presented. There, it is shown that the interfacial turbulence produces drops larger than 10 μm and large drops imply small specific interfacial area. This puts a constraint on the drop size distribution that we cannot overcome, unless we can induce another type of emulsification mechanism or apply much more energy. Nevertheless, we can try to explain the results which look interesting. Higher ionic strength reduces the interfacial turbulence [Miller, 1988]. This can explain why at higher alkali concentration, the interface expands the less. There are still several questions to be answered but we do not have the answers to them yet. For instance, why does the system emulsify less as it crosses certain pH limit? What does that pH limit means? Is it a critical condition? Can we some how induce another spontaneous emulsification mechanism without the help of another surfactant, but just by adjusting the salinity or adding small amount of NH_4OH to

the surfactant/oil system before mixing with enough water to reach the desired emulsion final composition?

Figure 4-4 shows that the salinity has an effect on the expansion of the specific interfacial area of the emulsion formed when a oleic-acid/hexadecane solution drop is injected in the Coulter sizer chamber filled with an aqueous solution containing NH_4OH at 4mM and at different salinities. Here, the specific interfacial area presents a maximum around a salinity of 4 mM. A maximum always suggest the competition of at least two factors. In this case, the salinity affects factors that enhance the expansion of the interfacial area as well as factors that oppose to the expansion of the interfacial area. Some of these factors are probably the interfacial tension and the interfacial turbulence.
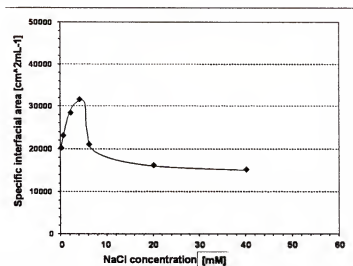
Figure 4-4. The specific interfacial area vs. salinity of the emulsion formed when a oleic-acid/hexadecane solution drop is injected into the Coulter sizer chamber filled with an aqueous solution of NH_4OH at 4mM.

4.3 Conclusions

The specific interfacial area test (SIAT) appears to be a powerful tool to asses the effect of different factors affecting the emulsion drop size distribution and emulsification mechanism.

Surfactant structure, surfactant concentration, surfactant to co-surfactant ratio, pH, and salinity are factors that affect the drop size distribution, the specific interfacial area and the spontaneous emulsification mechanism.

CHAPTER 5
A MOLECULAR MECHANISM TO SPONTANEOUSLY PRODUCE NANO-
EMULSIONS BY DESTABILIZING LAMELLAR LIQUID CRYSTALLINE PHASE

5.1 Introduction

Spontaneous emulsification phenomenon is an important technological tool to design emulsions with small drop size distribution (even of the order of nano-emulsions) [Becher, 1983; Forgiarini, 2000; Forgiarini, 2001; Groves, 1978; Lopez-Montilla, 2002a; Lopez-Montilla, 2002b; Miller, 1988; Ozawa, 1997; Pillai, 1999] and highly concentrated internal phase and low energy consumption formation [Forgiarini, 2000; Forgiarini, 2001; Miller, 1988; Ozawa, 1997]. This phenomenon has already found applications in fields such as self-emulsifying drug delivery systems (SEDDS) [Pouton, 1997; Wakerly, 1986], agriculture and pesticides [Becher, 1983; Rosen, 1972]. It also has potential application in many others field such as enhanced oil recovery (EOR) [Pillai, 1999; Rivas, 1997; Kanicky, 1999] and detergency [Forgiarini, 2001; Raney, 1987], among others.

The spontaneity and the mechanisms are probably the two most relevant characteristics of the spontaneous emulsification phenomenon. The spontaneity of the emulsification tells about the rate and the extension of the emulsion formation process. In a similar way the mechanism lead us to design emulsions with specific droplet size distributions. It can also be used to lower the energy consumption and to avoid the need for sophisticated devices to produce nano-emulsions.

In this chapter, a mechanism to produce nano-emulsion in Brij30/hexadecane/water systems is proposed and, in the next chapter, microscopic

observations that suggest that there is a correlation between spontaneous emulsification mechanism and emulsion droplet size are shown.

We propose a molecular mechanism, "Lamellar liquid crystal instability", for the spontaneous formation of nano-emulsion for Brij30/hexadecane/water systems. We hypothesize that the presence, or the formation, and subsequent destruction of lamellar liquid crystal phase in response to compositional changes is an essential requirement for spontaneous production of nano-sized droplets (60-300 nm) for Brij30/hexadecane/water systems. We also report here the "memory" associated with these mesomorphous structures, whereby a two step emulsification involving a liquid crystal phase can produce much smaller droplets as compared to one step emulsification. These statements are based on qualitative (video microscopy) and comparative quantitative measurements (Coulter Counter) of droplet size distribution and specific interfacial area at various temperatures and concentrations along the dilution line in the equilibrium phase diagram of Brij30/hexadecane/water ternary system. The emulsification interfacial area for these systems shows a maximum with respect to temperature and is centered around the Phase Inversion Temperature (PIT). Extensive spontaneous emulsification is favored by the increase in the concentration of surfactant in the system as long as the state of the system before dilution with water is in the liquid crystal state or just before liquid crystal phase formation (i.e., isotropic microemulsion).

If the system has already passed through the birefringent phase upon the addition of water or is far away from formation of the liquid crystal phase, then the dilution of such a system does not produce the spontaneous emulsification and does not yield ultrafine emulsions (i.e., nano-emulsions).

When a Brij30/hexadecane system is brought in contact with water, at high (>18/82 w/w) surfactant-to-oil ratio, the water penetrates into the oil phase forming a liquid crystal phase. As the time proceeds the water molecules continue diffusing inside the liquid crystal structure, thus separating its lamellas more and more until a critical distance (the so-called persistence length) is reached. After this moment, instabilities propagate throughout the outer lamellas inducing a massive destruction of the liquid crystal structures into nano-droplets. These instabilities keep on propagating toward the inner lamellas as more water diffuses inside the liquid crystal structure until the whole system is converted into a nano-emulsion.

5.2 Results and Discussion

Figures 5-1 shows the schematic of the pseudo ternary triangle phase diagram and the emulsification protocols followed in this study for the Brij30/hexadecane/water systems. This diagram shows the three components (surfactant, S; Oil, O; water, W) assigned respectively to any of the corner of the triangle, various single phase (sponge, L_3; w/o microemulsion, L_2; and lamellar liquid crystal, L_α) and multiphase (L_2+L_α, $L_\alpha+O$, and o/w microemulsion (L_1)+O) regions. The lamellar liquid crystal (L_α) zone extends from the surfactant-water edge towards the oil corner, the L_2 phase region runs along the surfactant-oil edge and the L_3 region is located in a small region under the L_α phase. The dilution lines (dashed lines) suggest the phase transition path of different systems may follow when they are brought in contact with water in a quasi-equilibrium manner. In this study, however, because the dilution process occurs in a non-equilibrium fashion, the systems may transiently undergo different phase transitions than that

suggested by the dilution lines depending on the surfactant-to-oil ratio and on the initial

water concentration.
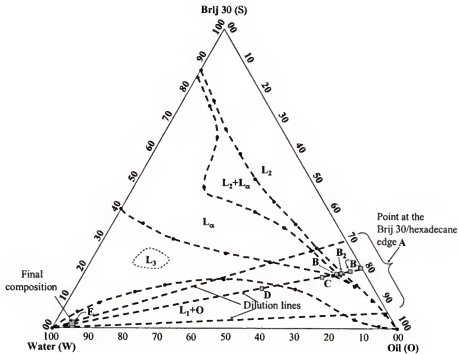
Figures 5-1. The schematic of the pseudo ternary triangle phase diagram and the
emulsification protocols followed in this study for the
Brij30/hexadecane/water system. This diagram shows the three components
(surfactant, S; Oil, O; water, W) at any of the corners of the triangle,
different single phase (sponge, L_3; w/o microemulsion, L_2; and lamellar
liquid crystal, L_α) and multiphase regions where some of the L_1, L_2, L_3, L_α,
and O phases can coexist. It also shows the schematic of the emulsification
protocols for the different systems studied. The dilution lines (dashed lines
on the phase diagram) connecting points A, B, C, D, to E represents the
spontaneous emulsification protocols. Points A, and B, C, and D
corresponds to the initial and medium states respectively and point E is the
final concentration reached when a drop of an initial or intermedium system
is injected and mixed with water into the Coulter sizer chamber.

The emulsification extent can be correlated to the emulsion specific interfacial

area [Lopez-Montilla, 2002b]. Similarly, the effect of the phase structure the

emulsification extent can be correlated to the emulsion specific interfacial area as well as

to the emulsion drop size distribution, the effect of phase behavior on specific interfacial

area and drop size distribution from phases prepared with incremental amounts of water along a dilution line were studied. Figure 5-2 shows the liquid crystal phase region and interfacial area for Brij30/hexadecane/water systems which compositions are located along six dilution lines. For systems with surfactant-to-oil ratios of 5/95 w/w and 10/90 w/w, the water concentration does not appear to affect the specific interfacial area much, which is almost constant for all water concentrations ($< 20,000$ cm^{2}mL^{-1}). For surfactant-to-oil ratios greater than 15/85 w/w, the interfacial area of the emulsions formed follows the trend (1) low interfacial area from surfactant-oil solutions, (2) transition from small to large interfacial area in the microemulsion phase (B_1), (3) a high interfacial area plateau in the liquid crystal region (B) and finally (4) a steep transition from high to low interfacial area again in the multiphase regions (C, D). With increasing surfactant-to-oil ratios, the width of the plateau region as well as the interfacial area for emulsification from liquid crystal phase is increasing. The width of the plateau region for interfacial area closely corresponds to the lyotropic stability (width of the dilution line segment crossing liquid crystal phase). Figures 5-3a – 5-3d show complementary information about the effect of phase structure on emulsification regarding the drop size distributions for systems in three different water regions, A, B, and C, of the phase diagram. As can be seen, the water concentration has an important effect on drop size distribution at all surfactant-to-oil ratios; however, for small surfactant-to-oil ratio (5/95 w/w), it is not enough to achieve sub-micron droplet sizes. These small droplet sizes (< 1 μm) can only be obtained when the surfactant-to-oil ratios are higher (i.e., $> 15/85$ w/w). It is also observed that the average droplet sizes change from large to very small to large again when one dilutes to composition E from compositions A, B and C respectively. It is

apparent that the systems that emulsify the most (i.e., small drop size) are initially in the region of lamellar liquid crystal phase, a phase that has been correlated with ultralow interfacial tension [Evans, 1994; Kellay, 1994; Miller, 1988; De Gennes, 1982]. Probably, the low interfacial tension between the lamellar liquid crystal phase and the contacting water induces the breaking of the thin lamellas of oil covered with surfactant molecules into nano-droplets.
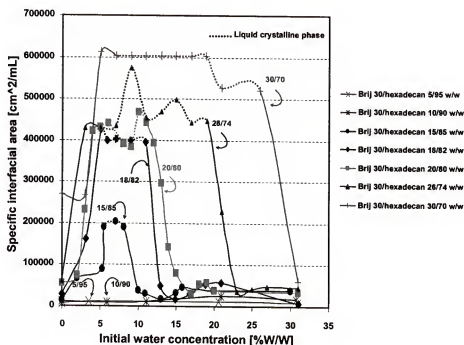
Figure 5-2. The combined effect of Brij30 to hexadecane ratio and the initial water concentration, at room temperature, on the specific interfacial area of the emulsion formed when 10μL of Brij30/hexadecane/water systems previously prepared are injected into the counter sizer chamber filled with 125 mL of water that is kept gently stirred. The Brij30 to hexadecane ratios and initial water concentration explored here are respectively 5/95, 10/90, 15/85, 20/80, 26/74, and 30/70 w/w and water concentration ranging between 0 and 30 % w/w.

For surfactant-to-oil ratios above 20/80 w/w, interfacial area from the microemulsion region B_1 (compositions closest to liquid crystal region but still isotropically clear) is comparable to that from corresponding liquid crystal region

suggesting both phases (disordered microemulsion phase vs. ordered liquid crystal phase) are equally important towards production of high specific interfacial area. We however believe that liquid crystal phase, due to its high lyotropic stability at these high surfactant-to-oil ratios, is the prime contributor for the observed high interfacial area, where in the dynamic process of emulsification (B_1 - E) it is very likely that those microemulsion phases immediately evolve into a liquid crystal phase. Microemulsion phases with small surfactant-to-oil ratios (e.g., 15/85 w/w) do not show large interfacial areas as during the mixing process, the system quickly moves to multiphase regions without evolving into a liquid crystal phase due to its low lyotropic stability.
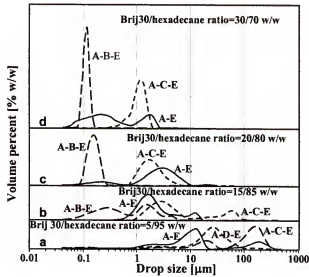
Figure 5-3. Differential volume weighted droplet size distributions of the Brij30/hexadecane/water systems for different water concentration at different surfactant-to-oil w/w ratios: Figure 5-3a describes the Brij30/hexadecane 5/95 w/w system at 0, 5, and 30 % w/w of initial water concentration; Figure 5-3b describe the Brij30/hexadecane 15/85 w/w system at 0, 5, and 30 % w/w of initial water concentration; Figure 5-3c describe the Brij30/hexadecane 20/80 w/w system at 0, 5, and 30 % w/w of initial water concentration; Figure 5-3d describes the Brij30/hexadecane 30/70 w/w system at 0, 20, and 30 % w/w of initial water concentration.

Among other factors, the emulsification protocol is one of the most important variables controlling the emulsion properties. In order to further prove that the presence of liquid crystal phase is the determining factor for the production of nano-emulsions the effect of the protocol on the specific interfacial area was studied. Figure 5-4 shows the schematic of the protocol and its effect on the specific interfacial area for Brij30/hexadecane/water systems along the 20/80 w/w surfactant-to-oil ratio dilution line.
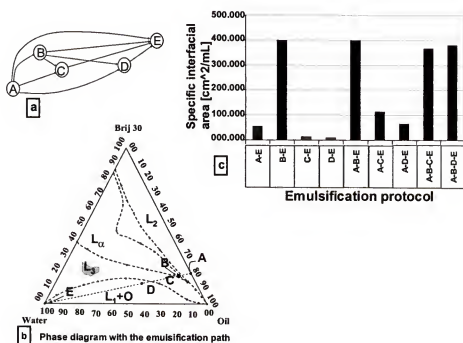
Figure 5-4.   The schematic of the protocol and its effect on the specific interfacial area when Brij30/hexadecane solutions prepared at 20/80 w/w ratio are mixed with water in different proportions. In Figure 5-4a a schematic diagram of the different paths follows by the system to reach the final point E starting from A is shown; Figure 5-4b shows the phase diagram with the different intermediate compositions and the segments of the dilution line tying them together. In Figure 5-4c it is showed the effect of the emulsification protocol on the specific interfacial area is shown.

Figure 5-4a is a schematic diagram of the different paths followed by the system to reach the final point E starting from compositions A, B, C, and D. Paths A-E, B-E, C-E and D-E are achieved by rapid mixing of Brij30, hexadecane, and water in appropriate

concentrations to reach the compositions A, B, C and D then equilibrating for 20 minutes before adding more water to reach the final composition E. The mixing is performed fast enough such that the systems do not have time to achieve any intermediate steady state. Paths A-B-E, A-C-E, A-D-E are achieved in the similar manner with the only difference that the starting system is Brij30/hexadecane (A). Figure 5-4b depicts the above trajectories on a triangular phase diagram. Figure 5-4c shows the effect of the emulsification protocol on the specific interfacial area. Here, once again it is clear that the emulsions with large interfacial area are those in which one of the intermediate states is a liquid crystal phase such as composition B. These results further corroborate our hypothesis that the presence of the liquid crystal phase is fundamental to the production of nano-droplets.

For a non-ionic surfactant temperature strongly affects the phase behavior. From this point of view temperature should have a strong effect on interfacial area for systems where the lyotropic stability is important (i.e., > 15/85 w/w). In Figure 5-5, the interfacial area at different temperatures is investigated for different surfactant-to-oil ratios. For all surfactant-to-oil ratios greater than 18/82 w/w, the specific interfacial area passes through a maximum as a function of temperature with the peak shifting to lower temperatures with increasing surfactant-to-oil ratio. The interfacial area of the systems with surfactant-to-oil ratios of 26/74 w/w and 30/70 w/w is strongly affected by the temperature. However, the interfacial area of systems with ratios of 20/80, 18/82 and 15/85 w/w, is moderately affected by the temperature, producing lower interfacial area emulsions. Furthermore, the interfacial area of the systems with ratios of 5/95 and 10/90 w/w is much less affected by the temperature. The systems that are most affected by the

temperature are those for which the width of the dilution line crossing the liquid crystal region is big (i.e., the higher the lyotropic stability, the larger the effect of the temperature on the interfacial area). This maximum in emulsification has normally been correlated to phase inversion temperature (PIT), a temperature around which the interfacial tension passes through a minimum and the curvature of the surfactant is close to zero [Evans, 1994; Kunieda, 1996; Ozawa, 1997].
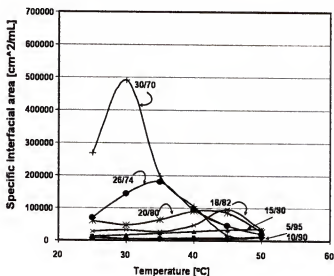
Figure 5-5. The combined effect of the surfactant-to-oil ratio and the temperature on the specific interfacial area of the emulsion formed when 10 μL of Brij30/hexadecane/water system is injected into the counter sizer chamber filled with 125 mL of water that is kept gently stirred. The Brij30 to hexadecane ratios and temperatures explored are respectively 5/95, 10/90, 15/85, 20/80, 26/74, and 30/70 w/w and 25, 30, 35, 40, 45, and 50 °C.

Figure 5-6 shows the effect of the surfactant-to-oil ratio on the phase inversion temperature (PIT). This plot shows that the PIT is strongly affected by the surfactant-to-oil ratio; the higher the surfactant-to-oil ratio the lower the PIT. The interfacial areas obtained by PIT method are either comparable (at 30/70 w/w) or lower (26/74 w/w and below) to those obtained by the destruction of a preformed liquid crystal phase at room

temperature implying that dilution from a liquid crystal phase is a better control for obtaining high interfacial area (low drop size) emulsions.
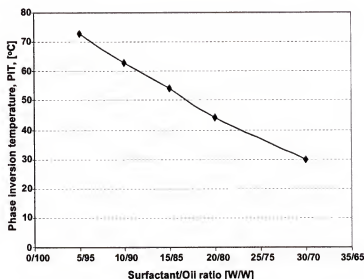
Figure 5-6. The effect of the Brij30- to-hexadecane ratio on the phase inversion temperature (PIT) at (surfactant/oil)-to-water ratio of 50/50 w/w.

Figures 5-7 Shows the photographical sequences of the different stages of the spontaneous emulsification process for the system Brij30/hexadecane/water at 20/80 w/w surfactant-to-oil ratio following path A-E, and A-B-E. Figure 5-7a shows the sequence of the initial stages of the spontaneous process when a drop of a Brij30/hexadecane solution (A) is brought in side-by-side contact with a drop of water. As soon as the drops touch each other, the water drop spreads on the top of the oil drop in an explosion-like process forming large drops (5 to 30 μm). Figure 5-7b shows the emulsification of a liquid crystal "drop" placed on the top of water column in a Petri dish; it is observed that the liquid crystal is throwing material away from it. An interesting observation is that regular strips of material peel off from the liquid crystal drop. Because of the regularity of the strip, we believe that this fracture has occurred along a lamella. We also noticed periodic explosion-like processes occurring on the outer surface of it throwing finely

divided material to the aqueous phase. These might be the microscopic lamellas that are exploding as a result of being swollen by water. Figure 5-7c shows the emulsification when a liquid crystal (point B) drop is placed on the bottom of a Petri dish that is subsequently filled with water. The drops in this case are so small that one can only see some dark streams of material rising from the liquid crystal drops. The photograph constitutes optical evidence that those systems on the liquid crystal region, B, mainly produce nano-size droplets, while the others produce large drops. Figure 5-7a shows that when the intermixing process is fast, part of the system does not undergo phase transition through liquid crystal thereby producing large drops. For this surfactant/oil ratio (20/80 w/w) the lyotropic stability is low (see Figure 5-1), meaning that when a system in composition A mixes with water, it could undergo phase transition from A to C, D or E without ever completely passing through the liquid crystal phase in between.

The mechanism we propose for small droplet formation from liquid crystal phase is on lines of De Gennes [1982] and is shown in Figure 5-8. Liquid crystal are ultra low interfacial tension phases form by elements or pieces of lamellas, of a small characteristic size call persistence lengths (ξ_k), which are joined together. Persistence length is a length scale over which the surface normal vectors are correlated (i.e., flat surface) under thermal fluctuations and it depends on the surface to volume ratio; it can also be seen as the size of the elements forming a particular phase. If persistence length (ξ_k) is greater than the inter-membrane distance, one expects stable liquid crystal phase but if it is smaller than inter-membrane distance, one expects wrinkled sheets, which can break by means of the thermal fluctuation motions forming isotropic, disordered liquid phases (e.g., microemulsions) of length scales ξ_k. In this respect, the water would induce

instabilities in the lamellas of a liquid crystal phase when they are brought in contact. The water penetrates in between the lamellas, thus increasing the inter-membrane distance and making it bigger than the persistence length, leading to the destruction of the lamellar liquid crystal phase into droplets of sizes on order ξk.
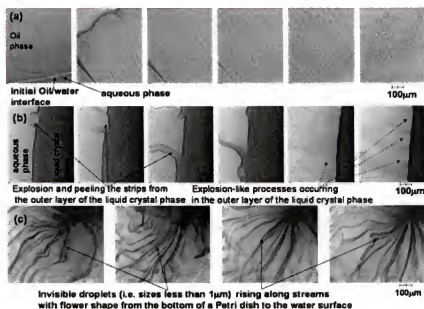
Figures 5-7. The photographical sequences of the different stages of the spontaneous emulsification process for the Brij30/hexadecane/water system at surfactant-to-oil ratio 20/80 w/w. In Figure 5-7a drop of a Brij30/hexadecane solution at 0 % of initial water concentration is brought in contact with a drop of water. In Figure 5-7b a liquid crystal drop is placed on the top of water content in a Petri dish. In Figure 5-7c a liquid crystal (point B) "drop" is placed on the bottom of a Petri dish which is then filled with water.

Finally, this study might be relevant in industrial applications such as agrochemical and pharmaceutical formulations. Many agricultural products (e.g., pesticides, insecticides and herbicides) consist of oils that must be diluted in water before use. When diluted, they must not only disperse easily without much agitation and form an emulsion of adequate stability, but they should also keep their characteristics until they are used. Therefore, self-emulsifying oils are highly suitable as vehicles for agricultural

products since as low as 1 % v/v of them is required to prepare the final mixture for the field application. In this way, manufacturers can avoid the transport of preformed emulsion, containing large amounts of water, to the farm from the industrial facility, which is both unnecessary and expensive. Accordingly, the active ingredient of these products is formulated in anhydrous oil (containing surfactants) that is conveniently transported. The oil concentrate can then be added to water from a local supply and sprayed at the point of application. The results from this research suggest that these concentrates should be prepared as a liquid crystal phase or in the microemulsion phase just before the formation of the liquid crystal phase.
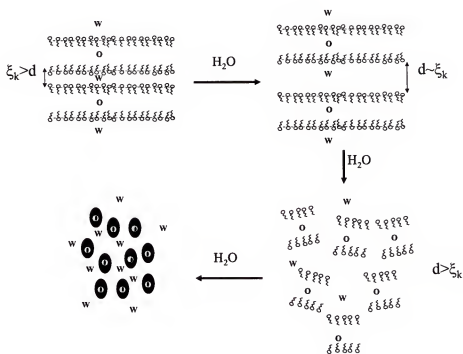
Figure 5-8.   The schematic of the proposed "Lamellar liquid crystal instability" mechanism.

5.3 Conclusions

From this study the following conclusion can be drawn:

Liquid crystal instability is the mechanism for the formation of nano-emulsion when Brij30/hexadecane/water systems are brought in contact with water. Thus, either the presence or the subsequent evolution to a liquid crystal phase is an indispensable requirement for the formation of nano-emulsions with very narrow drop size distribution.

For the production of nano-emulsion, the protocol path must always cross the liquid crystal phase.

The temperature plays an important role on the emulsion interfacial area for the systems for which the dilution line crosses the liquid crystal zone. At phase inversion temperature a maximum in the interfacial area is observed.

CHAPTER 6
SPONTANEOUS EMULSIFICATION MECHANISMS IN RELATION TO
EMULSION DROPLET SIZE

6.1 Introduction

Drop-size distribution is one of the most relevant characteristics of an emulsion. It can largely affect emulsion properties such as viscosity, stability, taste and color. Drop-size distribution can also affect mass transfer and reaction rates if the emulsion is used as a medium for liquid-liquid extraction or for chemical reaction. Thus, the control of the drop-size distribution is imperative. Considering this, some researchers have started to correlate emulsification protocol to emulsion mean drop-size as first approach to control the emulsion drop size distribution.

Here, I am trying to go a step forward, by establishing a correlation between the spontaneous emulsification mechanisms and the resulting emulsion-droplet size and drop size distribution. In chapter 1, I described the different spontaneous emulsification mechanisms that different researchers have proposed up to the date. In chapters 3, it was suggested that liquid crystal instability is the mechanism responsible for the production of submicron-size drops and in chapter 5 I presented the proof of this statement. In chapter 4, I have shown that a system (i.e., oleic-acid/hexadecane/ammonia-solution) that emulsify preferentially under the interfacial turbulence mechanism [Nishimi, 2001; Rudin, 1994] produce large drops (30 μm). In this chapter, as I did in the previous one, I show a correlation between spontaneous emulsification mechanisms and emulsion drop

size distribution. In order to achieve this objective, different systems under various phases were studied under various phases.

6.2 Results and discussion.

I proved in the previous chapter the occurrence of a spontaneous emulsification mechanism that produces droplets at submicron level. These kind of mechanisms where the droplets and the kind of instability occurs at submicron level, which is the limit of the optical microscope, cannot easily be determined by direct observation, but by using others alternatives techniques such as drop sizer. However, some mechanisms of spontaneous emulsification can easily be identified due to their main characteristics are visible under an enhanced video microscope with resolution at micron level.

Figures 6-1 present three photographical sequences and drop size distribution corresponding to the main mechanism occurring to a AOT/hexadecane solution drop when it is brought in contact with a water drop on the top of a microscope slide. In Figure 6-1a it is illustrated by means of photographical sequences three spontaneous emulsification mechanisms (1) interfacial turbulence, (2) Rayleigh instability and (3) negative (ultralow) interfacial tension. Immediately after a AOT/hexadecane solution drop contact water it starts to split into droplets of different sizes by means of different spontaneous emulsification mechanisms that occur simultaneously. In sequences a_1, the oil-water interface shakes with violent movements and eventually splits itself into drops of different sizes ranging from 20 to 80 μm. The violent movements of the interface referred as interfacial turbulence for this emulsification mechanism. Paying attention to this sequence it is observed that in less than 0.1s the interface changes the position and splits into drops several times. Sequences a_2 depict the main characteristics of the

Rayleigh instability mechanism. Here, the oil phase containing AOT in a slow motion

flow to the aqueous phase as a liquid jet where it detach from the main drop forming

drops of about 40 to 100 μm. In sequence a_3, smaller particles than in the other two cases

detach from the oil phase. Here, it is observed that a different phase is formed at the

interface and from it long and thin fingers of oil are flowing to the aqueous phase and

eventually detach from that interface. Figure 6-1b shows the drop-size distribution

obtains from the Coulter sizer. Interestingly, although, the conditions in the coulter sizer

chamber are really different from those in the microscope slide (i.e., there is much more

water and some energy is supplied by the stirrer), the results regarding drop size are very

close to each other. The system presents two modes about 4 and 35 μm respectively.

When the oil contacts the water phase, the surfactant molecules start to partition toward

the oil-water interface [Miller, 1988] and from there some surfactant molecules diffuse to

the water phase. The partition of AOT to the interface could be uneven due to its bulky

hydrophobic part, which induces several instabilities of the Marangoni-like phenomenon

[Davies, 1961a; Davies, 1957; Miller, 1988; Rudin, 1994] that gives to the interface

enough energy to shake and to split itself into large drops. Under the effect of a factor

like gravity, the difference in densities between the oil phase and the aqueous phase

together with relatively low interfacial tension can induce a second kind of instability.

Although a microscope slide is almost horizontal, once it is placed in the microscope

stage, the small level difference between the oil drop and the water drop could be enough

to induce the formation of small oil jets which undergo Rayleigh-like instability. The

uneven surfactant concentration at the interface and the density and level difference

between the oil and the aqueous phase can explain the existence of the first two

mechanisms. How is the third mechanism induced? In sequence a_3, I observed the presence of a new phase at the oil-water interface. This phase appears to be a liquid crystal since it looks very viscous in the microscope (i.e., the movements are slow and there is not much turbulence at the interface. It has been reported in the literature that the liquid crystal phases present very low interfacial tension [Chan, 1981; De Gennes, 1982; Kellay, 1994; Shah, 1980]. A very low interfacial tension together with the small level gradient between the oil and the aqueous phase discussed above explain the existence of those very thin threads coming out from the oil drop. As the time progresses not only the surfactant partition to the interface and to the water phase, but also the water partition to the oil phase, thus, inducing the formation of a liquid crystal phase [Miller, 1988, Nishimi, 2000]. As mention above, the low interfacial tension and the hydrostatic gradient give origin to this spontaneous emulsification mechanism.

a   b
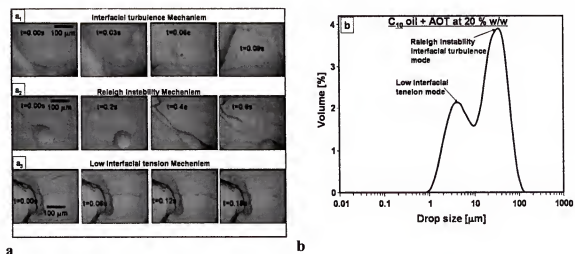
Figures 6-1. Photographical sequences of three spontaneous emulsification mechanisms that take place when a AOT/hexadecane solution, at surfactant to oil ratio 20/80 w/w, drop contacts a water drop and the resulting drop size distribution when a drop of the AOT system is injected into the Coulter sizer chamber. Figure 6-1a depicts the photographical sequences. Figure 6-1b shows the differential volume-weighted drop size distribution for the o/w emulsion of the AOT/hexadecane/water system.

Two other spontaneous emulsification mechanisms that frequently take place when a surfactant/oil phase contact water are diffusion and stranding (see chapter 1) and liquid crystal instability (see chapters 3 and 5). Figures 6-2 illustrates the main characteristics of the spontaneous emulsification process of a Brij30/hexadecane system through a photographical sequence taken by means of an enhanced videomicroscope under cross polarized light and its drop size distribution obtained from the Coulter sizer. Figure 6-2a illustrates some of the most important characteristics of the diffusion and stranding mechanism. When a Brij30/hexadecane drop (at 20 % w/w of surfactant concentration) is brought in contact with a water drop, the water drop moves on the top of the oil drop in a process that resembles an explosion. In this process, the water drop sweeps most of the oil, thus, moving the water-oil interface towards the left hand side. After few seconds, the thin layer of oil that got trapped under the aqueous phase nucleates into oil drops of sizes around 0.8 to 80 μm. As the time progresses, more number of drops appear which later get surrounded by a bright layer. Furthermore, the water-oil interface also becomes shiny. Although it is not clear in the photograph, most of the drops formed during this spontaneous process must be 1 μm or smaller because what one can see is just some uniform and opaque material detaching from the region just before the bright interface. Figure 6-2b illustrates the drop size distribution of the emulsion formed when a Brij30/hexadecane solution drop is injected into the Coulter sizer. This system presents a roughly bimodal distribution with modes around 0.2 μm and 2 μm.

The photographical sequences and the size distribution show that this system emulsifies under two mechanisms, one producing very small drops, and the other large droplets. However, in opposite to the above case, the most of the drops in the

photographical sequences appear to be larger than the drops around the mode II presented in the distribution. As mentioned about, the conditions in the Coulter chamber are really different from those in the microscope slide. As one can observed in last photograph, all the drops are surrounded by a bright layer. This layer is a lamellar liquid crystal [Kunieda, 1996; Ozawa, 1997] that at the microscope slide conditions (i.e., low water concentration) can exist and surround the drops. However, in the Coulter chamber there is much more water than in the microscope slide which does not allow existence of the equilibrium between a liquid crystal phase and an aqueous phase (see point E in Figure 5-1). When an oil drop is injected in the coulter chamber, the liquid crystal that may form around the new formed drops will immediately disintegrate into tiny drops [Nishimi, 2000]. This explains why the largest drop in the distribution has smaller size than those observed in the microscope. Furthermore, as discussed in chapter 5, when a drop of a composition A mix with water to reach the composition E (see Figure 5-1), it does not necessarily form liquid crystal phase (i.e., if the mixing process is very fast, the system composition will cross the liquid crystal region composition before it self-assembles into a liquid crystal structure). This explains why two modes and not one mode at 0.3 µm exist in size distribution curve.

The photographical sequences and the size distribution show that this system emulsifies under two mechanisms, one producing very small drops, and the other large droplets. However, in opposite to the above case, the most of the drops in the photographical sequences appear to be larger than the drops around the mode II presented in the distribution. As mentioned about, the conditions in the Coulter chamber are really different from those in the microscope slide. As one can observed in last photograph, all

the drops are surrounded by a bright layer. This layer is a lamellar liquid crystal [Kunieda, 1996; Ozawa, 1997] that at the microscope slide conditions (i.e., low water concentration) can exist and surround the drops. However, in the Coulter chamber there is much more water than in the microscope slide which does not allow existence of the equilibrium between a liquid crystal phase and an aqueous phase (see point E in Figure 5-1). When an oil drop is injected in the coulter chamber, the liquid crystal that may form around the new formed drops will immediately disintegrate into tiny drops [Nishimi, 2000].

Figure 6-2. Photographical sequences of three spontaneous emulsification mechanisms that take place when a Brij30/hexadecane solution, at surfactant to oil ratio 20/80 w/w, drop contact a water drop and the resulting drop size distribution when a drop of the Brij30/hexadecane system is injected into the Coulter sizer chamber. Figure 6-2a depicts the photographical sequences whereas Figure 6-2b shows the differential volume-weighted drop size distribution for the o/w emulsion of the Brij30/hexadecane system after contacting water.

The about arguments explain why the largest drop in the distribution has smaller size than those observed in the microscope. Furthermore, as discussed in chapter 5, when a drop of a composition A mix with water to reach the composition E (see Figure 5-1), it

does not necessarily form liquid crystal phase (i.e., if the mixing process is very fast, the system composition will cross the liquid crystal region composition before it self-assembles into a liquid crystal structure). This explains why two modes and not one mode at 0.3 µm exist in size distribution curve.

There are two other ways to produce nano-drops (1) by thermal instability of a liquid crystal and (2) by destabilizing a bicontinuous microemulsion. As mentioned in the chapter 5, a liquid crystal can be destabilized by increasing its temperature or by diluting it with water or with oil. On the other hand, a bicontinuous microemulsion can be destabilized by bringing it in contact with another phase which is not at equilibrium with it. Figure 6-3 shows the drop size distribution of the Brij30/hexadecane/water system at surfactant to oil ratio of 30/70 % w/w and at 20 % w/w initial water concentration. Here, one can observe that the distribution become narrower and the mode become smaller as the temperature reaches the PIT (see chapter 5).
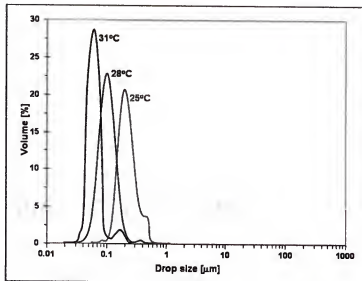

Figure 6-3.   Volume-weighted drop size distribution of the emulsion produced when a Brij30/hexadecane/water liquid-crystal "drop" is brought in contact with water.

Furthermore, the liquid crystal structure is formed by a puzzle of small pieces that can break off from the structure when the layer are swollen with water [De Gennes, 1982; Kellay, 1994] or with oil [Shahidzadeh, 1997] or when thermal energy is given to the system [De Gennes, 1982; Kellay, 1994]. Those small pieces have a characteristic length that changes, among others, with the solvent and with the temperature [De Gennes, 1982; Kellay, 1994]. Once those tiny pieces are dispersed into a phase they become nano-droplets. In this case as the temperature increases the persistence length decreases and the droplets become smaller.

Figure 6-4 shows the emulsion drop size distribution formed when a bicontinuous microemulsion is brought in contact with water. This system forms emulsion with a bimodal drop size distribution. The smaller mode is located around 0.1μm whereas the larger one is located around 3 μm. A bicontinuous microemulsion is a self-assembly structure like a liquid crystal. It is not strange that a similar mechanism that breaks a liquid crystal structure into tiny pieces also breaks a bicontinuous microemulsion into nano-drops when it is destabilized. In this case the microemulsion is formed by SDS, amyl alcohol, dodecane and brine (see Table2-1). The salinity of this microemulsion is relatively high, 3.6%, which induces the surfactant salting out effect (i.e., makes the surfactant to partition a phase different than water). When such microemulsion contact pure water, the surfactant, which is very hydrophilic, partitions to the aqueous phase. Along this process, the surfactant changes its curvature from zero to positive towards the aqueous phase. These changes in the surfactant affinity and curvature must induce a strong instability throughout the whole microemulsion making the system to become nano-emulsion. Since in a bicontinuous microemulsion, the oil to water ratio is around

1:1, it is not strange that part of the oil strand after some surfactant and alcohol diffuse to the aqueous phase and undergo changes on their curvature forming a mode around 2 to3 μm.
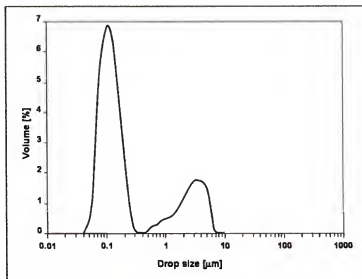
Figure 6-4. Volume-weighted drop size distribution of the emulsion produced when a middle-phase-microemulsion drop (see Table 2-1) is brought in contact with water.

6.3 Conclusions

Each spontaneous emulsification mechanism split the oil phase into their characteristic droplet size distribution. The Rayleigh instability produces the largest drops (0.4 μm) whereas the liquid crystal instability the smallest ones (0.1 μm).

The temperature can shift the characteristic mode produced by liquid crystal instability. As the temperature approaches to the PIT, the mode decreases in favor smallest size (0.1-0.3 μm) droplets.

THREE PROTOCOLS TO INDUCE SPONTANEOUS DETERGENCY THUS INCREASING BOTH THE DETERGENCY EFFICIENCY AND EFFICACY

7.1 Introduction

Spontaneous emulsification is a phenomenon that has found applications in several technological fields such drug delivery systems, pesticide and cutting oils. This phenomenon becomes suitable to all of those cases where a large liquid-liquid interfacial area it is required, and the production of emulsions in place and/or with low energy consumption. In the following two chapters, two important applications of the spontaneous emulsification phenomenon that were developed during my time in the Dr. D. O. Shah's laboratory will be presented.

In this chapter, I propose that the presence of an oil soluble non-ionic surfactant (Brij30) in an oil stain, or addition of it through an oil-based solution or water-based mixture to the stain, enhances to a great extent the spontaneous removal of the stain from a polyester fabric by inducing rollback and spontaneous emulsification phenomena. UV-vis spectroscopy is used to analyze the effect of the surfactant structure, the surfactant concentration, and the protocol for applying the surfactant to the stained fabric on the removal of an oil stain composed of mineral oil plus orange OT.

Increased economic incentives for energy conservation have stimulated research aiming to develop new surfactant systems, and to a lesser extent, to identify surfactant-application protocols that can reduce the time required to remove soil from fabrics and

hard-surface substrates. One of the goals of this research is to identify and induce effective mechanisms of detergency for these applications.

There are at least three principal mechanisms for removal of liquid soils by surfactants [Rosen, 1982]. First, the rollback mechanism is where in presence of a strongly wetting surfactant solution thin layers of oily soil on the surface to be cleaned retract to form drops. This mechanism depends on the wetting properties of aqueous surfactant solutions. The drops either detach spontaneously, if the surfactant solution spreads over the entire surface, or are broken off by the agitation that occurs during the ensuing washing process. The second mechanism is emulsification where a thick layer of an oily liquid breaks into drops. This process requires either that the emulsion form spontaneously, or that the available agitation be capable of deforming the oil-water interface to the extent that individual drops break off. The existence of low interfacial tension facilitates the breaking off of the individual drops from the interface of the soiled solid substrate [Raney, 1987]. Finally, the third mechanism is where the oil solubilizes into the core of the micelles or into a more easily removable intermediate phase. This mechanism may take place when organic liquid or organic solid materials are the soil [Raney, 1987; Rosen, 1982]. The soil can be directly solubilized into the surfactant micelles [Carroll, 1981; Shaeiwitz, 1981]. Alternatively, the soil may form an intermediate phase containing soil, surfactant, and water that is more readily removed than the original soil, for instance, by direct emulsification. A common intermediate phase is a lamellar liquid crystal [Lawrence, 1959; Raterman, 1984]. There is no information available on whether the formation of certain types of intermediate phases is favorable or unfavorable for soil removal.

A rollback is widely believed to be the dominant mechanism for high-temperature washing of cotton fabrics with common anionic detergent formulations [Raney, 1987; Rosen, 1972]. However, soils that are rapidly removed by rollback at high washing temperatures that cause a low viscosity may require subsequent removal by solubilization at low temperatures. Moreover, rollback is inherently more difficult to achieve when the adhesion between soil and fabric is strong, as is the case with oily soils on many synthetic fabrics.

On the other hand, it is believed that rollback is not the primary detergency mechanism for nonionic surfactants [Raney, 1987]. Furthermore, nonionic surfactants are also generally less hydrophilic than the ionic surfactants that are typically used in detergency. The solubilization mechanism is probably more appropriate for describing the detergency effects under non-ionic surfactants, given that they remove soil effectively only when micelles are present [Rosen, 1972]. In contrast, anionic surfactants are typically effective even at concentrations well below the critical micelle concentration, presumably because their adsorption on the fabric and the resulting rollback do not require the presence of micelles [Schott, 1972]. Photographs of experimental observations have shown that there are no significant changes in contact angle during the solubilization of oil drops on Teflon fibers by nonionic surfactant solubilizations. Soil removal by nonionic surfactants from synthetic fabrics correlates better with the oil-water interfacial tension than with the contact angle, and is most favorable for the lowest interfacial tension [Pierce, 1980]. Furthermore, for nonionic surfactants, the solid-water interfacial tension does not contribute significantly to soil removal, although a reduction in the surface tension is usually considered to be the driving factor causing rollback

[Dillan, 1979; Dillan, 1980; Rosen, 1972]. Nevertheless, rollback seems to be the dominant detergency mechanism of oil removal from horizontal surfaces immersed in surfactant solutions; in fact, visual observations easily confirm that oil drops break off from the solid surface. Reduction in the oil-water interfacial tension could lead to gravitational (Raleigh-Taylor) instability of interfaces, such as those where the oil underlies a denser surfactant solution [Davies, 1957]. Low interfacial tension also facilitates emulsification by agitation.

In contrast to the established notions discussed above, the experimental study that I present here indicates that rollback can be the primary mechanism for detergency when using the nonionic surfactant Brij30 if the surfactant is either dissolved in the oil phase or dispersed in the aqueous phase at a concentration higher than 23 mM. In this research, I investigate the effect of the surfactant, the surfactant concentration, and the protocol of surfactant application on the detergency of mineral oil from a polyester fabric. It is shown that, for the system studied, Brij30 provides superior detergency than sodium SDS and Brij35.

A most significant finding of this research is that I have shown that it is possible to spontaneously remove up to approximately 85% of oil from an oil-stained fabric. It must be noted that the term "spontaneously" implies that there is little-to-no application of an external force to aid the removal process.

7.2 Results and Discussion

The quantitative results of the spontaneous detergency for the removal of mineral oil-orange OT from a polyester fabric by means of different surfactants (Brij30, SDS, and Brij35) are summarized in Figures 7-1 to 7-3. The combined effects of surfactant, surfactant concentration, and surfactant application protocol on the kinetics of the

detergency process are shown in Figures 7-1a to 7-1f, while Figures 7-2 and 7-3 are "cuts," at 20 minutes, of Figures 7-1c, 7-1e, and 7-1f ; and Figures 7-1a to 7-1d, respectively.
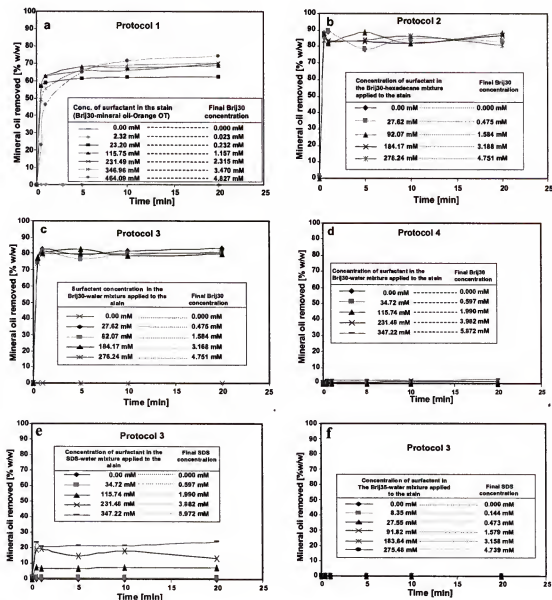
Figures 7-1. The effect of the surfactant structure, surfactant concentration, protocol, and time on oil removal from a polyester fabric. Figures 7-1a to 7-1d present the effect of Brij30 under the protocols 1, 2, 3 and 4, respectively, on the removal of mineral oil from a polyester fabric along time. Figures 7-1e and 7-1f indicate the effect of the SDS and Brij35 concentration, respectively, under the protocol 3 on the mineral oil removal from a polyester fabric with time.

Four important facts regarding the spontaneous removal of mineral oil from a polyester fabric can be observed from Figures 7-1 to 7-3 (1) the process is very fast, and in a few seconds most of the systems reach equilibrium conditions (i.e., the detergency process is complete, see Figures 7-1). (2) The surfactant plays a main role; Brij30 is more effective than the others two surfactant (i.e., SDS and Brij35, see Figure 7-2). (3) Brij30 concentration seems to reach a critical concentration value around 23 mM, below it the removal of mineral oil is extremely poor, and above which an increase in concentration does not appear to significantly increase the detergency efficiency (see Figures 7-1 to 7-3). On the other hand, such a critical concentration is not observed in the case of SDS, where the concentration has a proportional effect on the detergency process (i.e., the higher the concentration, the higher removal of oil), nor in the case of Brij35, which does not appear to be a good detergent for mineral oil removal (see Figure 7-2). (4) The protocol is an outstanding factor controlling the detergency performance (see Figure 7-3).
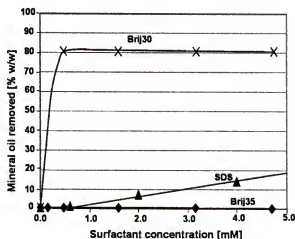

Figure 7-2. A cut of the Figures 7-1c, 7-1e, and 7-1f at 20 minutes. It illustrates the combined effects of surfactant structure, and surfactant concentration on mineral oil removal under protocol 3 from polyester fabric achieved in 20 minutes.
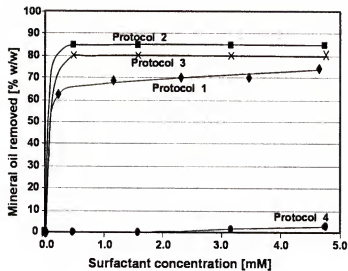
Figure 7-3. A cut of the Figures 7-1a to 7-1d at 20 minutes. It illustrates the combined effects of Brij30 concentration and protocol on mineral oil removal from polyester fabric achieved in 20 minutes.

Protocols 1, 2 and 3 are the most effective. In all three of them, before adding the washing water, the surfactant concentration around the stain is high. Under Protocol 4, in contrast, the surfactant concentration around the stain is never high, even though the final surfactant concentration is the same as in the other three cases.

Oily soils are removed by emulsification, solubilization, or rollback mechanism [Rosen, 1972; Herrera, 1996; Thompson, 1994]. In this case, it seems that the spontaneous emulsification and the rollback phenomena are the predominant detergency mechanisms. The high solubility of Brij30 in an oil phase makes it partition to the oily stain, thus inducing spontaneous emulsification [Lopez-Montilla, 2002] and rollback (see Figures 7-4). These phenomena are concentration-dependant, especially the spontaneous emulsification [Forgiarini, 2001; Rosen, 1972]. At low surfactant concentration, (approximately between 23 and 115 mM), the predominant detergency mechanism is rollback; while at high concentration it is spontaneous emulsification.

In order to determine the factors controlling the detergency mechanisms a drop of the Brij30/mineral-oil/orange-OT system is placed on a hydrophobic surface, and then is brought in contact with water and observed microscopically through an enhanced video microscope. The photographical sequences obtained show that the spontaneous detergency process occurs by means of a spontaneous emulsification and of a rollback phenomenon. Figures 7-4 show photographical sequences of the spontaneous detergency process occurring when a Brij30/mineral-oil/orange-OT drop previously placed on a surface is brought in contact with water. The sequences of Figures $7\text{-}4a_1\text{-}7\text{-}4a_6$ shows that at 464.09 mM of Brij30 concentration the water washes out part of the oil as soon as contact is established. Several processes take place simultaneously: first, the formation and immediately rollback of an intermediate phase (probably liquid crystal) that seems to induce the disintegration and posterior removal of part of the remaining oil by spontaneous emulsification leaving just a thin oil film spread on the solid surface and; second, the rollback mechanism takes place one more time and induces the remaining thin oil film to evolve into an oil droplet which finally detaches from the solid surface, see Figures $7\text{-}4a_7\text{-}7\text{-}4a_{12}$. It also appears that the oil drop undergoes phase transition before it detaches. Figures $7\text{-}4b_1\text{-}7\text{-}4b_6$ shows that even at 231.49mM the Brij30/mineral-oil/orange-OT system still undergoes a phase transformation when it is brought in contact with water. As above, the new phase seems to be easily spontaneously washed out from the solid surface. Finally, from Figures $7\text{-}4c_1\text{-}7\text{-}4c_6$ I can say that at low surfactant concentration (i.e., less than 115.75mM) rollback is the predominant.

The photographical evidence presented in Figures 7-4 reveals that when the surfactant is dissolved in the oil phase it promotes different phenomena that are

concentration-dependent (i.e., rollback, phase transformation, and spontaneous emulsification), and that they culminate with the spontaneous detergency of an oily soil.

Finally, it is important to stress that the conclusions of this research open new possibilities for approaching the cleaning of oil from hard surfaces. There are numerous situations where it is difficult to clean-up surfaces, especially if there are many grooves or if presents dangerous conditions during the cleaning process. For all of those types of surfaces, spontaneous detergency holds significant potential for becoming a suitable cleaning solution.

7.3 Conclusions

The surfactant structure, surfactant concentration, and the protocol are the most important factors affecting oil removal from a polyester fabric. Brij30 proved to be the most effective detergent among the surfactants studied. It was also shown that in order for the Brij30 to be effective, it must be applied at concentrations close to 23.20 mM or greater. At lower concentrations, the removal efficiency was very poor, and at higher concentrations, the removal efficiency exhibited minimal, if any, improvement (Figure 7-2). Protocols 1, 2, and 3 were effective in spontaneously removing the oil stain, whereas Protocol 4 was very inefficient. It is also important to mention that the kinetics of the spontaneous detergency process is fast (i.e., in less than 1 minute the process appears to reach full completion). It was shown that the detergency mechanism can be tailored by manipulating the surfactant structure and surfactant concentration.

The results show that three factors namely the surfactant type, surfactant concentration, and the application protocol are very important for detergency of mineral oil, and that the kinetics for the spontaneous detergency is very fast.
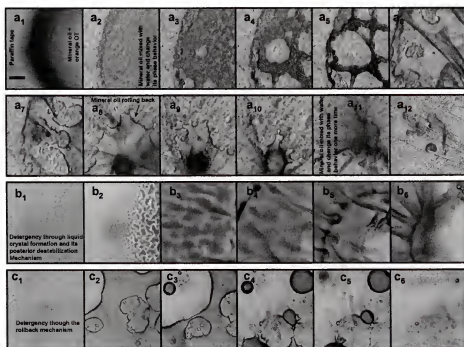
Figures 7-4. Several photographical sequence of the spontaneous detergency process occurring when a Brij30/mineral-oil/orange-OT drop previously placed on substrate-surface contacts water. In Figures 7-4a_1 to 7-a_{12} a Brij30/minera-oil/orange-OT solution drop, at 464.09 mM, placed on paraffin tape in the bottom of a Petri dish is brought in contact with water. Figures 7-4b_1 to 7-4b_6 and 7-4c_1 to 7-4c_6 a Brij30/mineral-oil/orange-OT solution drop, at 231.49 and 115.75mM, respectively, placed on the bottom of a plastic Petri dish which is brought in contact with water.

CHAPTER 8
WATER PURIFICATION

8.1 Introduction

Aromatic compounds play an important role in chemical production processes. In addition, because of their intensive use, aromatics often appear as undesired pollutants in process water from which they have to be removed before the water can be used again or delivered into the environment [Venter, 2001]. However, separation of aromatics like phenolic compounds from water is difficult due to their low relative volatilities and to their tendency to form azeotropes and eutectics [Hoshi, 2000; Niesner, 2000; Venter, 2001]. The desired water purification from phenolic compounds cannot therefore be achieved by means of conventional distillation processes [Hoshi, 2000; Niesner, 2000].

Several processes have been designed to remove these aromatic molecules from process water, among them liquid-liquid extraction appears to be one of the most promising methods in achieving this difficult job. When two or more immiscible liquid phases, which are not in equilibrium, are brought in contact, they exchange materials due to the component chemical potential gradients between two phases. The mass transfer process for any given compound continues until its chemical potential in the different co-existing phases is the same.

In the surfactant/co-surfactant/oil/brine systems, several bulk phases and interfaces can co-exist at equilibrium. This and the fact that many of the aromatic molecules have strong affinity for the surfaces and interfaces or for the oil phase strongly

suggest the possibility of using these systems in liquid-liquid extraction process to remove aromatic hazardous molecules from water.

8.2 Extraction of Pollutants

In this chapter, I propose two methods for the removal of aromatics hazardous molecules (e.g., phenol) from water based on the liquid-liquid extraction process.

8.2.1 Method 1

In method 1, water source having hazardous molecules is formulated with surfactant, co-surfactant, oil and brine to produced systems of two or three phases (i.e., Winsor II and III systems [Salager, 1983], see Figure 8-1). The formulated system is then mixed forming a nano-emulsion that keeps the water and the oil in close-contact along a huge interfacial area facilitating the mass transfer between the phases as well as among the phases and the interface. Few minutes after the mixing process is stopped, the emulsion separates into its constituting phases, thus, achieving the desired separation of the hazardous molecules from water.

8.2.2 Method 2

In method 2, water containing hazardous components is brought in contact with a bicontinuous or a w/o microemulsion which spontaneously produce an o/w emulsion which provides an enormous number of droplets and a huge interfacial area between the oil and the aqueous phases. As was said above, these nano-domains and the huge interfacial area provide suitable conditions for the mass transfer process among the phases and between the phases and the interface. After the phases have been in contact for some time, enough to reach the equilibrium conditions, the nano-emulsion is destabilized by adding aluminum salt and then the resulting dispersion is filtrated by means of a 200 nm mesh filter.

The principle of these two liquid-liquid extraction methods lies on the two following facts. First, some hazardous materials have strong selective interactions with medium chain length alcohols, surfactants and/or with oils. Second, surfactant molecules provide the conditions to generate large water-oil interfacial area by producing a huge numbers of oil nano-domains. Surfactants drive the alcohol molecules (surface-active molecules) to such interfaces and also keep those nano-domains separated from each others. In this way, surfactant molecules can be seen as alcohol and oil sequestrators. Hence, the separation of the surfactant rich phase from the aqueous phase (i.e., migration of surfactant to a middle phase microemulsion, to a top phase microemulsion or to a precipitated solid phase, see Figure 8-1) would then mean the removal of the hazardous molecules from the water.

This study was aimed at elucidating the role of solvent and co-surfactant as driving forces on the removal of pollutant molecules by swollen micelles and droplets.

8.2.3 Phase Diagram: A Powerful Tool for Designing Separation Methods

The phase diagram of a surfactant/co-surfactant/oil/brine system is a powerful tool in designing liquid-liquid separation process. Figures 8-1 illustrates the general schematic of the pseudo-quaternary phase diagram for the (surfactant/alcohol)/oil/brine systems. In Figure 8-1a, the surfactant/alcohol, oil and brine phases are placed at the corners of the diagram and the salinity correspond to the vertical axis. As the concentration of the different components vary, the phase behavior and the orientation of the tie line changes. Having in mind a phase diagram, as shown in figure 8-1a, one can think for method 1 that an aqueous solution containing hazardous material at composition B' can be formulated together with surfactant, alcohol, oil, and brine to reach the composition A or E and E". At equilibrium, systems at compositions A and E separate

into 3 phases whereas systems at composition E" separate into two phases. These phase separations, have the wonderful consequence of the partial or total removal of the undesired material from the water. The method 2 can be visualized as one in which an aqueous solution with a pollutant at composition B' is brought in contact with a system at composition C or C' forming an emulsion at composition E'. Figure 8-1b shows three horizontal cuts of the Figure 8-1a at low, optimal and high salinity. This figure illustrates the traditional triangular phase diagram for Winsor-like systems. Here, the number of phases as well as the orientation of tie lines changes as the salinity of the system shift from low to high passing through the optimal salinity. A two-phase region is presented at low and high salinity while three two-phase regions and a three-phase region are presented at optimal formulation. At low salinity, an o/w microemulsion is in equilibrium with an oil phase whereas at high salinity an aqueous phase is in equilibrium with a w/o microemulsion. Systems at optimal salinity present three two-phase regions and a three phase region; on the left hand side, two-phase region represents the equilibrium between a bicontinuous microemulsion and an aqueous phase, the right hand side, two-phase region represents the equilibrium between a bicontinuous microemulsion and an oil phase, the bottom two-phase region represent the equilibrium between an aqueous phase and an oil phase and, finally, the three-phase region represent the equilibrium among an aqueous phase, a bicontinuous microemulsion and an oil phase.

8.4 Results and discussion

To study the role of different solvents on the extraction of green Bromocresol from water, several systems were analyzed (see Figure 8-2a). Figure 8-2a qualitatively shows the effect of the extracting solvent on the removal of green Bromocresol from water. For the systems studied, amyl alcohol and nonionic surfactants appear to be the

most effective solvents for the extraction of green Bromocresol. Figure 8-2b

qualitatively shows the schematic of the general phase behavior of the

(surfactant/alcohol)/oil/brine systems. As the salinity increases, the surfactant affinity

changes from hydrophilic to hydrophobic, which makes these systems evolves according

to the Winsor's system [Salager, 1983] from a two-phase system (with an o/w

microemulsion in the bottom in equilibrium with an oil phase in the top) to a three-phase

system (with an aqueous phase in the bottom in equilibrium with a bicontinuous

microemulsion in the middle and with and an oil phase in the top) to a two-phase system

(with an aqueous phase in equilibrium with a w/o microemulsion in the top) (see Figures

8-1). The color of the different phases indicates that the green Bromocresol follows the

microemulsion phase. The formulations for the different microemulsion systems

prepared are found in Tables 2-1 to 2-4.
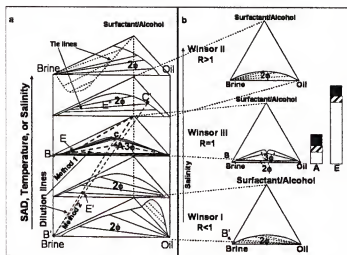
Figures 8-1. The schematic of a general (surfactant/alcohol)/oil/brine phase diagram with
the protocols and phase transition the system may undergo. Figure 8-1a
shows a phase diagram with the two protocols to study. Figure 8-1b
illustrates transversal cuts of figures 8-1b at low, optimum and high salinity.
It also shows how the compositions A and E would look-like. Here SAD
represents the surfactant affinity difference between the oil phase and the
aqueous phase.
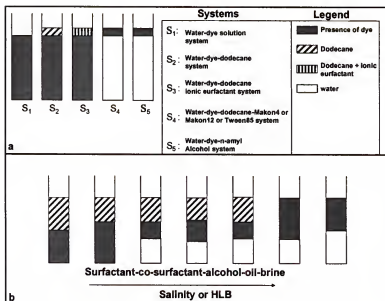
Figures 8-2. Effect of different solvents and phases on the removal of green Bromocresol from water. Figure 8-2a qualitatively depicts the effect of different solvents on the removal of green Bromocresol from water. Figure 8-2b shows how the salinity of the (surfactant/alcohol)/oil/brine system increases migration of the dye to the middle and the top phases as it increases.

Figure 8-3 shows the quantitative validation of the two methods presented here to remove hazardous molecules from water, in this case green Bromocresol. Figure 8-3a illustrates the impressive removal of about 100 % of green Bromocresol from water by formulating the polluted water with surfactant, alcohol, oil and brine to reach a three-phase system (method 1). All of the studied systems (see Tables 2-1 to 2-4) removed more than 99 % of the dye from the original polluted water. Figure 8-3b shows the removal of green Bromocresol from water by using the liquid-liquid extraction method 2 in which 25 mL of aqueous solution containing dye at 1000ppm are mixed with different volumes (0.25, 0.5, 1, 1.5, 2 and 2.5) of bicontinuous microemulsion of SDS (see section 2.4.8 for more experimental details). The curve describing the removal of dye present two zones which are differentiated by their slops. The first zone is characterized by a steep decrease in dye concentration in water achieved by a small volume (from 0 to 2.5

mL) of microemulsion. This section of the curve indicates that a small volume of

microemulsion can remove great percent (up to 75%) of the dye from water. A second

zone is depicted by an almost flat section of the curve, which indicates that extra addition

of microemulsion does not help in the removing of dye as the first zone does.

Nevertheless, 2.5 mL of SDS microemulsion is enough to removed more than 98 %w/v

of the dye. Probably, the reason for the large change in the slope is that at low dye

concentration, the mass transfer obeys another equilibrium low (i.e., as the concentration

of the dye in water decreases, a first order mass transfer rate can shift two a second order

one, etc.). For this reason, the extraction of dye at low concentration would require the

use of fresh microemulsion (i.e., in order to enhance the efficiency of the extracting

process, one should work in multistage manner using 0.25mL of middle phase each time).
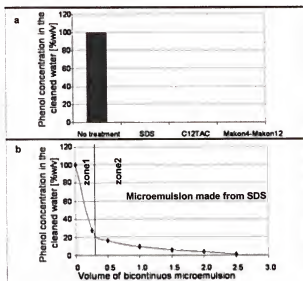
Figures 8-3. Effect of different microemulsions on the removal of green Bromocresol
from water. Figure 8-3a quantitatively illustrates the effect of different
middle phase microemulsion phases on the removal of green Bromocresol
from water. Figure 8-3b shows the effect of the volume of the (SDS/n-
Amyl- alcohol)/brine middle-phase microemulsion on the removal of green
Bromocresol from water by following the protocol 2.

Before continuing, it is important to say that the method 1, although very efficient for the removal of green Bromocresol and probably other materials, it also pollutes the water because of the high salinity required to formulate most of these systems. On the other hand, the method 2 does not pollute the water very much and still can removed the hazardous material. In this respect, it is important to say that aluminum salts are use to in water treatment.

Removal of green Bromocresol from water can be considered an "easy task", since its solubility in water is very low (although it shows a very strong color). However, the removal of molecules likes phenol (i.e., phenol is soluble in water at 1g per 15 mL of water and harmful at very low concentration less than 20 part per million, ppm) can be a challenging task. In this respect, to separate phenol at concentration of few ppm from water one may not only require of interfacial co-solvents like alcohols, as in the case of green Bromocresol, but also require polar oils that can induce a driving force for the diffusion of phenol from the aqueous phase to the interface and to the oil phase as well.

Figures 8-4 illustrates the effect of oil phase as well as the surfactant on the removal of phenol from water. In Figure 8-4a, it is observed that dodecane, a hydrophobic oil, does not remove phenol from water. The removal of phenol considerably increases as the hydrophilicity of the oil increases from dodecane to ethyl oleate to ethyl butyrate. Figure 8-2b illustrates the effect of the surfactant charge on the removal of phenol from water; here, stearyl trimethylammonium chloride ($C_{18}TAC$), a cationic surfactant, shows a much better performance than SDS on the removal of phenol from water. These two remarkable results can be explained in the sense of interaction among the molecules. Oils like ethyl butyrate and ethyl oleate have oxygen on their

structures which provide suitable conditions for hydrogen bond interactions with the hydrogen present in the phenol molecule. It is also very likely that the phenol ring interact with those oxygen atoms present in the oil. In the case of the surfactants, $C_{18}TAC$ a positive charged surfactant will interact stronger with phenol than SDS a negatively charged surfactant since the oxygen and the aromatic ring in the phenol molecules can be consider as having a negative character.
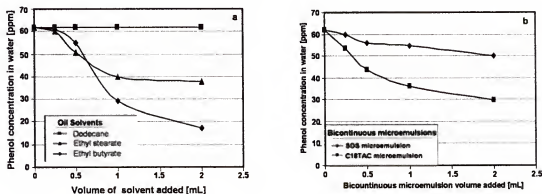

Figure 8-4. Effect of solvents on the removal of phenol from water. Figure 8-4a illustrates the combined effect of the volume and surfactant of two middle phase microemulsion on the removal of phenol from water by following the protocol 2. Figure 8-4b shows the combine effect of the volume and nature of three different oils on the removal of phenol from water after shaking the phenol/oil/water system for ten minutes and leaving it to rest for two days.

The above results suggest that to separate phenol from water one should use microemulsion system form by ethyl butyrate and a cationic surfactant. However, the precipitation of the nano-emulsion stabilized by cationic surfactant bring additional problems like the used of ionic surfactants to induce the separation of the nano-domains that have trapped the phenol molecules. To avoid this problem, I decided to study the synergism on the removal of phenol from water induced by microemulsion containing SDS and ethyl butyrate. A w/o microemulsion made from SDS, amyl alcohol, ethyl butyrate and brine provides a large interfacial area for mass transfer, a simple

precipitation mechanism (i.e., anionic surfactant precipitate with aluminum salts) and the conditions to trap the phenol molecules (because of the presence of ethyl butyrate).

The above results suggest that to separate phenol from water one should use microemulsion system form by ethyl butyrate and a cationic surfactant. However, the precipitation of the nano-emulsion stabilized by cationic surfactant bring additional problems like the used of ionic surfactants to induce the separation of the nano-domains that have trapped the phenol molecules. To avoid this problem, I decided to study the synergism on the removal of phenol from water induced by microemulsion containing SDS and ethyl butyrate. A w/o microemulsion made from SDS, amyl alcohol, ethyl butyrate and brine provides a large interfacial area for mass transfer, a simple precipitation mechanism (i.e., anionic surfactant precipitate with aluminum salts) and the conditions to trap the phenol molecules (because of the presence of ethyl butyrate).

Figures 8-5 show the effect of the oil present in a w/o microemulsion and the contrast oil vs. microemulsion on the removal of phenol from water. In Figure 8-5a, it is observed that the presence of ethyl butyrate in the w/o microemulsion has a tremendous impact on the removal of phenol from water. Whereas from Figure 8-5b, it is clear that for small volume, the microemulsion greatly enhances the removal of phenol from water as compare to the plain oil. As expected from the results presented in Figure 8-4a, a microemulsion made from ethyl butyrate removed more phenol than that made from dodecane due to the interaction between phenol and the oil. It was also expected that the microemulsion would remove more phenol from water than the plain oil due to its large interfacial area which is suitable for mass transfer. This expectation became true for small volume. However, for large volume both systems would remove almost the same

amount of phenol. As in the case of the dye, at low phenol concentrations, the extracting process follows another equilibrium law.
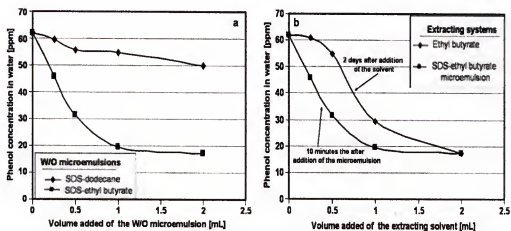

Figure 8-5.   Effect of solvents on the removal of phenol from water. Figure 8-5a illustrates the combined effect of the volume and oil structure of two w/o microemulsions on the removal of phenol from water by following the protocol 2. Figure 8-5b shows the contrast of using as extracting solvent a microemulsion made with ethyl butyrate vs. using the plain oil (ethyl butyrate) on the removal of phenol from water.

It is desirable to remove the maximum of phenol with a minimum of microemulsion volume. However, the above results show that there is a limit, probably set by the chemical equilibrium. In order to efficiently remove phenol from water, it would require a multistage separation process. Figure 8-6 presents a process that suggests the contrast between one stage vs. two stages separation process. For instance, using 1 mL of microemulsion to remove phenol from 25 mL of aqueous solution containing phenol at 62 ppm concentration would leave about 19 ppm of phenol in water. On the other hand, 0.5 mL of microemulsion would decrease the phenol concentration in the water to about 30 ppm and a second addition of 0.5 mL of microemulsion after a first filtration of the aqueous solution would leave the water with less than 10 ppm of phenol in the water which is a very good improvement.
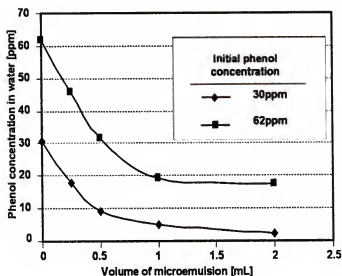
Figure 8-6.   Phenol concentration vs. volume of o/w microemulsion added to purify the water for two initial phenol concentrations in water (30 ppm and 62 ppm).

Finally, I will say that the take-home message from this research is that the method 1 could be very useful tool to study the effect of different physicochemical factors on the removal of pollutant from aqueous or from oil phases and method 2 looks very promising as a tool to remove hazardous material from water sources.

The next step would be using the method 1 to rank the factors in the removal of viruses (30nm particles) from water and using the method 2 as industrial technique to remove viruses from water sources.

8.5 Conclusions

Both methods have been shown to be promising for the removal of hazardous material from an aqueous solution. Although, specialized solvents must be used to trap these hazardous materials. In this respect, the alcohol group proved to be a good solvent to extract green Bromocresol whereas ethyl butyrate did the same for phenol.

It appears that a multistage process can be much more efficient than a single stage process for the removal of green Bromocresol and phenol from water.

CHAPTER 9
SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

9.1 Summary

9.1.1 A New Method to Quantitatively Determine the Spontaneity of the Emulsification Process

Traditionally, the spontaneity of the emulsification process had been determined by qualitative methods, CPAC test, and indirect methods based on properties such as turbidity, and electric conductivity. In this work, I presented a new method to quantitatively determine the spontaneity of the emulsification process. This method is based on the specific interfacial area, which is an essential characteristic of the emulsion systems which can describe the emulsification process. The emulsification process can be defined as one in which two immiscible liquid are mixed and one of them is dispersed into the other in the form of droplets. As the emulsification process progress the drops become smaller until they reach equilibrium conditions (i.e., the drops reach conditions in which they do not change the size). As the drop become smaller the interfacial area grows. In this respect, the monitoring of the interfacial area can be seen as the monitoring of the emulsification process. The importance of this method "specific interfacial area (SIAT)" lies on its ability to describe the emulsification process rate and extent, and on its capability to correlate the factors affecting the emulsification with the resulting emulsion properties. This method can also be used to characterize some of the spontaneous emulsification mechanisms. It also can help in designing formulations for emulsion products such as salad dressing, skin care product, and pesticide.

9.1.2 Spontaneous Emulsification Mechanisms: Liquid Crystal Instability

Spontaneous emulsification is a phenomenon that occurs through different mechanisms. The spontaneous emulsification mechanism can be of great help in describing the spontaneous emulsification phenomenon and the driving force that induce it. In this work, I proposed a mechanism "the liquid crystal instability" to explain the formation of nano-emulsion via liquid crystal. The lamellar liquid crystal phase can be the key to produce nano-emulsions with very low energy consumption. In this sense, this part of my research have revolutionary potential on technological applications. For instance, understanding the liquid crystal instability mechanism could help in formulating pesticide and skin care creams. Normally, the pesticides are formulated as concentrate oils, with not water in it to avoid phase separation, volume storage problem, or transportation of large volumes of liquids. However, I have shown that adding small amount of water to the concentrated oils can strongly affect the specific interfacial area (i.e., the drop size distribution) of the emulsion made out from them which in turns affect their effectiveness as pesticide.

9.1.3 Correlation between Spontaneous Emulsification Mechanisms and Emulsion Drop Size Distribution

Drop-size distribution is one of the most relevant characteristics of an emulsion. It can largely affect emulsion properties such as viscosity, stability, taste and color. Drop-size distribution can also affect mass transfer and reaction rates if the emulsion is used as a medium for liquid-liquid extraction or for chemical reaction. Thus, the control of the drop-size distribution is imperative. I established a correlation between the spontaneous emulsification mechanisms and the resulting emulsion-droplet size and drop size distribution. In chapter 1, I described the different spontaneous emulsification

mechanisms that different researchers have proposed up to the date. In chapters 3, it was suggested that liquid crystal instability is the mechanism responsible for the production of submicron-size drops. In chapter 5, I presented the proof of this statement. In chapter 4, I have shown that a system (i.e., oleic-acid/hexadecane/ammonia-solution) that emulsify preferentially under the interfacial turbulence mechanism [Nishimi, 2001; Rudin, 1994] produce large drops (30 μm). In chapter 6, I showed a correlation between spontaneous emulsification mechanisms and emulsion drop size distribution. In general, it was shown that the instabilities induced to the structures on self-assembled systems such that liquid crystal and bicontinuous microemulsion lead to the formation of emulsions with nano-size drops (< 1 μm). On the other hand, instabilities induced to interfaces of the hydrodynamic kind such as Raleigh-like instabilities or interfacial turbulence lead to emulsion with large-drops (1-100μm). Finally, chemical instabilities such as diffusion and stranding produce emulsion with medium drop size (1 to 20 μm).

9.1.4 Applications of the Spontaneous Emulsification Phenomenon: Detergency and Water Treatment

Spontaneous emulsification is a phenomenon that has found applications in several technological fields such drug delivery systems, pesticide and cutting oils. This phenomenon becomes suitable to all of those cases where a large liquid-liquid interfacial area is required, and/or the production of emulsions in place and/or with low energy consumption. I investigated the feasibility of using the spontaneous emulsification phenomenon to enhance the detergency of oil soil and the liquid-liquid extraction of hazardous molecules (e.g., phenol and green Bromocresol) from water.

9.1.4.1 Detergency

Increased economic incentives for energy conservation have stimulated research aiming to develop new surfactant systems, and to a lesser extent, to design surfactant-application protocols that can reduce the time required to remove soil from fabrics and hard-surface substrates.

In this sense, I identified two mechanisms (i.e., the spontaneous emulsification and rollback) that are involved in the spontaneous detergency and the factors (surfactant type, and concentration) controlling and inducing these mechanisms. For instance, I showed that the presence of an oil soluble non-ionic surfactant (Brij30) in an oil stain (mineral oil plus orange-OT), or addition of it through an oil-based solution or water-based mixture to the stain, enhances to a great extent the spontaneous removal of the stain from a polyester fabric by inducing rollback and spontaneous emulsification phenomena. The spontaneous removal of oil achieved was in the order of 80 %.

9.1.4.2 Water Purification

Aromatic compounds play an important role in chemical production processes. In addition, because of their intensive use, aromatics often appear as undesired pollutants in process water from which they have to be removed before the water can be used again or delivered into the environment [Venter, 2001]. However, separation of aromatics like phenolic compounds from water is difficult due to their low relative volatilities and to their tendency to form azeotropes and eutectics [Hoshi, 2000; Niesner, 2000; Venter, 2001]. The desired water purification from phenolic compounds cannot therefore be achieved by means of conventional distillation processes [Hoshi, 2000; Niesner, 2000].

In the surfactant/co-surfactant/oil/brine systems, several bulk phases and interfaces can co-exist at equilibrium. This and the fact that many of the aromatic

molecules have strong affinity for the surfaces and interfaces or for the oil phase strongly suggest that liquid-liquid extraction process are suitable to remove aromatic hazardous molecules from water.

I showed that spontaneous emulsification can induce the formation of nano-emulsion (i.e., systems with a large interfacial area). These systems can largely enhance the effectiveness of the liquid-liquid extraction process, since, they provide an extraordinary large interfacial area, which is one of the most important characteristics that determine the mass transfer process. In this sense, I showed that the nano-emulsions are excellent medium to removed hazardous material from the water source. It was also shown that the oil molecular structure is a main characteristic to take into account for the removal effectiveness. For instance, it was shown that ethyl butyrate is much better solvent than dodecane in the removal of phenol.

It is also important to say that some molecules can be used to indirectly drive the removal of hazardous molecules from source water. An example of this is the use of n-amyl alcohol to induce the removal of green Bromocresol in more than 80% from water. In this case, the surfactant molecules drive the alcohol molecules from water to the oil phase and in this way the alcohol molecules, which are molecules that present a strong interaction with green Bromocresol molecules, can now act to trap the hazardous molecules in the oil phase removing it from the water. This principle can be used in order to design systems for the removal of others hazardous molecules.

9.2 Recommendations for Future Work

The understanding of the different aspects of the spontaneous emulsification phenomenon is not yet complete. Recommendation for further research and development are giving below.

Polymer-surfactant systems constitute an upcoming area of interest. The ability of surfactant-polymer systems to induce synergism in producing emulsions with high stability can be combined to induce highly stable nano-emulsions.

The synergism effect of cationic-anionic surfactant systems to induced ultralow interfacial tension is an important factor to consider in order of improving the description of the spontaneous emulsification mechanisms. In this sense, I propose that this systems need to be investigated to progress in the understanding of spontaneous emulsification phenomenon. In the same way, anionic-nonionic or cationic-nonionic systems need also further investigation.

The feasibility of applying nano-emulsion systems in drug detoxification should be investigated. The incidence of patients with drug overdose has become a wide-world problem that has to be solved. Nano-emulsions seem to be promising in helping in lowering the risk of decease for this reason due to the fast rate and efficiently of drug up taking that these systems can achieve.

I recommend building a master plot that shows the functionality between the characteristics affecting the spontaneous emulsification phenomenon and the resulting values of the emulsion characteristics.

It should be investigated the feasibility of produce emulsion of any average drop size with a very narrow drop size distribution. I suggest that this can be achieved by combining the use of a solid membrane, of specific porosity, with spontaneous emulsification. This proposal is schematically represented in the Figure 9-1 and the schematic of the emulsion drop size distributions that can be obtained are presented in Figures 9-2.

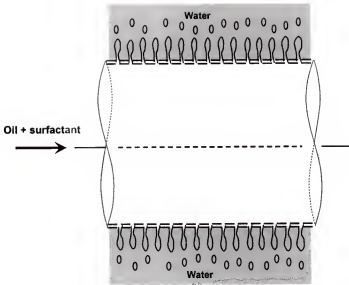Figure 9-1. Schematic of the emulsion produced by combining both spontaneous emulsification phenomenon and solid membrane technology.
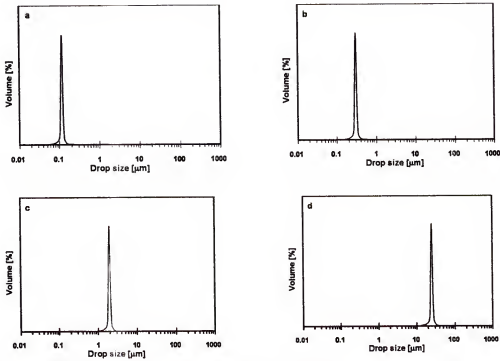

Figure 9-2. Schematic of the possible drop size distributions that can be obtained by combining spontaneous emulsification phenomenon and membrane technology. Figures 9-2a to Figures 9-2d show the drop size distributions at (a) 0.1 μm, (b) 0.3 μm, (c) 2 μm, (d) 25μm, respectively.

APPENDIX
SPONTANEOUS EMULSIFICATION SYSTE

Table A-1. List of some systems where spontaneous emulsification has been probed. Systems are ordered by application.

Systems • Two phase contacting: (1) aqueous phase//(2) oleic phase Surfactant-co-surfactant /water-salt-base//surfactant-co-surfactant/oleic phase • Two systems contacting: {1}//{2}	Temperature (°C)	Application
1-pentanol/water–KOH//stearic acid/n-hexadecane	15 to 55	-----
AOT/water–NaCl//linear alkanes (C_8, C_{10}, C_{12})	-----	-----
{C8phenol-9-EO}//{emulsion made of water//C9phenol-1,5-EO+C9phenol-4-EO / n-octane}	15 to 55	-----
{C9phenol-10-EO }//{emulsion made of water// C9phenol-1,5-EO+C9phenol-4-EO /n-decane}	15 to 55	-----
{C9phenol-9-EO}//{emulsion made of water// C9phenol-1,5-EO+C9phenol-4-EO /n-hexadecane}	15 to 55	-----
Dilute amine oxide surfactant/water//short-chain alcohol/n-decane	-----	-----
Dodecylammonium chloride/water//(cyclohexane or toluene or mesitylene or xylene)	-----	-----
DTAB/water//cetyl alcohol/toluene	20	-----
Ganglioside GM3/water–NaCl//oil	7 to 50	-----
Neodol 25-7/water//C12E8/n-decanol	35 and 45	-----
SDS/water//1-pentanol/tolune	15 to 55	-----
SDS/water//cholesterol/n-hexadecane	-----	-----
SDS/water//oleic acid	32	-----
SDS/water–NaCl//DDAO/n-decane	15 to 55	-----
Sodium cetyl sulfate/water//(cetyl alcohol or cholesterol or elaidyl alcohol or oleyl alcohol) /Nujol	-----	-----
Sodium decyl sulphate/water–KCl–KH2PO4//cetyl alcohol/toluene	20	-----
Sodium octyl sulphate/water–NaCl//cetyl alcohol/toluene	20	-----
Tergitol 15-S-7/water//C12E8/n-decanol	30 and 35	-----
Tris buffer solution//C12E8/n-dodecane	40	-----
Water//(PNE/PFE and Arylan PWS/Ethylan D254)/(cyclohexane or heptene or hexane or toluene)	25	-----
Water//acetic acid/toluene	20	-----
Water//AOT/n-hexane	-----	-----
Water//Brij30/n-hexadecane	25	-----
Water//C12-alkyl benzene sulfonic acid/white mineral oil	20	-----

Systems • Two phase contacting: (1) aqueous phase//(2) oleic phase Surfactant-co-surfactant /water-salt-base//surfactant-co-surfactant/oleic phase • Two systems contacting: {1}//{2}	Temperature (°C)	Application
Water//C12E5-n-dodecanol/ linear alkanes (C₈, C₁₆)	-----	-----
Water//C12E6-n-octanol/n-hexadecane	-----	-----
Water//C14DMAO-n-heptanol/n-decane	30	-----
Water//(C16 or C20 or C21 or C22-alkyl benzene sulfonic acid)/white mineral oil	20	-----
Water//diglycol laureate/Nujol	-----	-----
Water//ethanol/toluene	20	-----
Water//Imwitor 742-Tween 80/oil	-----	-----
Water//methanol/toluene	20	-----
Water//Polysorbate 80-Sorbitan monooleate/(benzyl alcohol or Dimethicone 1000 or isopropyl myristate)	25	-----
Water//potassium resinate-water/Hercolyn D rosin ester (b)	25 and 60	-----
Water//propanol/toluene	-----	-----
Water/sodium salt of EDTA//C12E4-Ninate 401-A/n-octane	50	-----
{Water} {Water-NaCl//AOT//(2,2,4-trimethyl pentane or n-decane or n-octane)}	30	-----
Water-NaOH//carboxilic acid/toluene	25	-----
Dodecylamine hydrochloride/water//p-xylene	25, 40 and 50	Asphalts
Water//C12E6-oleyl alcohol/n-hexadecane	30	Cosmetics
Water//C12E4-n-decane (a)	20, 30 and 50	Cosmetics, foods, aviation fuels and emulsion explosives
Water-NaCl//C12E6/monolaurin and n-decane (a)	5-50 and 20-50	Cosmetics, foods, aviation fuels and emulsion explosives
Water//Brij 30/n-decane	25	Cosmetics, nano-emulsion formation
Water//C12E4/n-hexadecane	20 to 70	Detergency
Water//C12E4/n-hexadecane and squalane	20 to 70	Detergency
Water//C12E5/n-hexadecane	20 to 70 and 50	Detergency
Water//C12E5/n-hexadecane and squalane	20 to 70	Detergency
Petronate TRS 10-80/water-NaCl//Brent and Dunlin crudes	22	Enhanced Oil Recovery
SDS/water//cholesterol/hexane	22	Foods
Water//C12E5-isooctanol/isooctane	-----	Low energy consumption and nano-emulsion formation
SDS/water//cetyl alcohol/toluene	20 and 65	Nano-emulsion formation
Water//PFE-PNE/n-hexane	25	Pesticides
Saline//Campul MCM90-Myverol 18-92-Chremophor EL/(Myvacet or Captex200)	37	SEDDS
Saline//Capmul MCM90-Centrophase 31-(Cremophor EL or Tween 80)/Captex 200	37	SEDDS
Saline//Capmul MCM90-Tween 80/Captex 355	37	SEDDS
Saline//Centrophase 31-Cremophor EL/Captex 200	37	SEDDS
Saline//Dicaprin-Centrophase31-Cremophor EL/Captex 200	37	SEDDS

Systems		
• Two phase contacting: (1) aqueous phase//(2) oleic phase Surfactant-co-surfactant /water-salt-base//surfactant-co-surfactant/oleic phase • Two systems contacting: {1}//{2}	Temperature (°C)	Application
Saline//Dicaprin-Centrophase31-Cremophor EL/Captex 200	37	SEDDS
Water-HCl//Tween 80/Imwitor 742	25 and 37	SEDDS
Water//Labrafac CM-10-Labrasol-lauroglycol/Myvacet 9-45 and Captex 200	-----	SEDDS
Glycerol monooleate/water//glycerol monooleate/Bridgelock TM	35	SEDDS
Phospholipids/water//phospholipids/Bridgelock TM	35	SEDDS
Polysorbate 80/water//Polysorbate 80/Bridgelock TM	35	SEDDS
Water//Tagat TO/Miglyol 812	40 and 60	SEDDS
Water//Tween 85/(Miglyol 812 or Miglyol 840)	40, 60 and 25	SEDDS
Water//Capmul MCM 90-Polysorbate 80/Peanut oil and Neobee oil	37	SEDDS
Water//Nonylphenol (5 or 6 or 8 or 9 or 10) Ethoxylate/(Miglyol 812 or Arachis Oil)	25 and 37	SEDDS
Water//polyoxyethylene (13.6) dioleate/(Miglyol 812 or Arachis Oil)	25 and 37	SEDDS
Water//polyoxyethylene (6.8 or 9.1 or 13.6) monooleate/Miglyol 812 or Arachis Oil	25 and 37	SEDDS
Water//Tagat TO or Tween 85)/(Arachis Oil or Miglyol 812)	25-40	SEDDS
Water//Labrafac CM (10 BM 287 or 6 BM 290 or 8 BM 284)/Peanut oil and Neobee oil	37	SEDDS
Water//Labrafac Hydro/Peanut oil and Neobee oil	37	SEDDS
Water//Labrafil M 10 BM 355/Peanut oil and Neobee oil	37	SEDDS
Water//Labrafil M 1944 CSD/Peanut oil and Neobee oil	37	SEDDS
Water//Labrafil M 2125 CS/Peanut oil and Neobee oil	37	SEDDS
Water//Labrafil NA 10 BM 369/Peanut oil and Neobee oil	37	SEDDS
Water//Labrafil WL 2609 BS/Peanut oil and Neobee oil	37	SEDDS
Water//PEG-25 glyceryl trioleate/Peanut oil and Neobee oil	37	SEDDS
Ethanol/water-NH4OH//tetraethoxysilane	23	Synthesis of submicron spherical colloids of titania-doped silica

(Adapted from Lopez-Montilla et al., [2002a])

LIST OF REFERENCES

Bataller, H.; Dicharry, C.; Lachaise, J.; Graciaa, A., "Formulation of Model Cutting-oil Water Emulsions Using Parafinic Oil and Ionic/nonionic Surfactant Mixture," Journal of Dispersion Science and Technology 2000, **21** (5), 571-588.

Baviere, M.; Canselier, J. P., "Microemusion in Chemical EOR Processes," in Industrial Applications of Microemulsions, Solans, C.; Kunieda, H. Eds.; Marcel Dekker, Inc., New York, 1997.

Becher, D. Z., "Application in Agriculture," in Encyclopedia of Emulsion Technology, 1st. Ed.; Becher, P. Ed.; Marcel Dekker, Inc., New York, 1983.

Bender, A. E.; Bender, D. A., in A Dictionary of Food and Nutrition; Oxford University Press, 1995.

Brand, H. R.; Pleiner, H., "Transient Orientation Order and Transient Positional Order in the Sponge (L3) Phase," Physica A: Statistical Mechanics and its Applications 2002, **312** (1-2), 79-85.

Buchannan, M.; Egelhaaf, S. U.; Cates, M.E., "Dynamics of Interface Instabilities in Nonionic Lamellar Phases," Langmuir 2000, **16** (8), 3718-3726.

Campbell, T. C., "The Role of Alkaline Chemicals in Oil Displacement Mechanisms," in Surface Phenomena in Enhanced Oil Recovery, Shah, D. O. Ed.; Plenum Press, New York and London, 1981.

Carroll, B. J. "The Kinetics of Solubilization of Non-Polar Oils by Non-Ionic Surfactant Solutions," Journal of Colloid and Interface Science 1981, **79** (1), 126-135.

Chan, K. S.; Shah, D. O., "The Physico-Chemical Conditions Necessary to Produce Ultralow Interfacial Tension at the Oil/Brine Interface," in Surface Phenomena in Enhanced Oil Recovery, Shah, D.O. Ed.; Plenum Press, New York and London, 1981.

Constantinides, P. P., "Lipid Microemulsions for Improving Drop Dissolution and Oral Absortion: Physical and Biopharmaceutical Aspects," Pharmaceutical Research 1995, **12** (11), 1561-1572.

Davies, J. T.; Haydon, D. A., "Spontaneous Emulsification," Proceedings of International Congress of Surfactants Act. 2nd 1957, **1**, 417-425.

Davies, J. T.; Rideal, E. K., "Diffusion through Interfaces," in Interfacial Phenomena, 1st. Ed.; Haram, W. Ed.; Academic Press, Inc., New York, 1961a.

Davies, J. T.; Rideal, E. K. "Disperse Systems and Adhesion," in Interfacial Phenomena, 1st. Ed.; Haram, W. Ed.; Academic Press, Inc., New York, 1961b.

De Gennes, P. G.; Taupin, C., "Microemulsions and the Flexibility of Oil/Water Interfaces," Journal of Physical & Colloid Chemistry 1982, **86**, 2294-2304.

Dillan, K.W.; Goddard, E. D.; McKenzie, D. A., "Examination of the Parameters Governing Oily Soil Removal from Synthetic Substrates," Journal of the American Oil Chemists Society 1980, **57** (7), 230-237.

Dillan, K.W.; Goddard, E. D.; McKenzie, D. A., "Oily Soil Removal from a Polyester Substrate by Aqueous Non-ionic Surfactant Systems," Journal of the American Oil Chemists Society 1979, **56** (1), 59-70.

Egbogah, E. O.; Dawe, R. A., "Spontaneous Emulsification Aspect of Enhanced Oil Recovery," Journal of Chemical Technology and Biotechnology 1985, **A 35** (3), 132-144.

El-Aasser, M. S.; Lack, C. D.; Vanderhoff, J.W.; Fowkes, F. M., "The Miniemulsificaton Process-Different Form of Spontaneous Emulsification," Colloids and Surfaces 1988, **29** (1), 103-118.

Evans, D. F.; Wennerstrom, H. "Bilayer Systems," in The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology Meet, VCH publishers Inc., 1994a.

Forgiarini, A.; Esquena, J.; González, C.; Solans, C., "Formation of Nano-emulsions by Low-Energy Emulsification Methods at Constant Temperature," Langmuir 2001, **17** (7), 2076-2083.

Forgiarini, A.; Esquena, J.; González, C.; Solans, C., "Studies of the Relation Between Phase Behavior and Emulsification Methods with Nanoemulsion Formation," Progress in Colloid & Polymer Science 2000, **115**, 36-39.

Förster, T.; von Rybinski, W.; Wadle, A., "Influence of Microemulsion Phases on the Preparation of Fine-Disperse Emulsions," Advances in Colloid and Interface Science. 1995, **58**, 119-149.

Gomati, R.; Bougurra, N.; Gharbi, A., "Correlation between the Fluidity and Topology of a Sponge Phase," Physica B: Condensed Matter 2002, **322** (3-4), 262-269.

Gommper, G.; Schick, M., "Scattering from Internal Interfaces in Microemulsion and Sponge Phases," Physical Review E 1994, **49** (2), 1478-1482.

Granek, R.; Ball, R. C.; Cates, M. E., "Dynamics of Spontaneous Emulsification," Journal of Physique II 1993, **3**, 829-849.

Green, P. J. "Binders," in Asphalts Surfacings, 2nd Ed.; Nicholls, J.C. Ed.; E & FN Spon, 1998, 47-78.

Greiner, R. W.; Evans, D. F., "Spontaneous Formation of a Water-Continuous Emulsion from a W/O Microemulsion," Langmuir 1990, **6** (12), 1793-1796.

Groves, M. J. Spontaneous Emulsification. Chemistry and Industry 1978, **12**, 417-423.

Groves, M. J.; de Galindez, D. A., The Self-Emulsifying Action of Mixed Surfactants in Oil," Acta Pharmaceutica Suecica 1976, **13**, 361-372.

Groves, M. J.; Mustafa, R. M. A., "Measurement of the "Spontaneity" of Self-Emulsifiable Oils," Journal of Pharmacy and Pharmacology 1974, **26**, 671-681.

Hellweg, T., "Phase Structures of microemulsions," Current Opinion in Colloid & Interface Science 2002, **7** (1-2), 50-56.

Herrera, C. G., "Detergency. Its Main Mechanisms," Grasas y Aceites 1996, **47** (6), 419-435.

Hoshi, M.; Ieshige, M.; Saitoh, T.; Nakagawa, T., "Separation of Aqueous Phenol Through Polyurethane Membranes by Pervaporation. III. Effect of the Methylene Group Length in Poly(alkylene glycols)," Journal of Applied Polymer Science 2000, **76** (5), 654-664.

Kanicky, J. R.; Lopez-Montilla, J. C.; Pandey, S.; Shah, D.O., "Application of Microemulsions in Enhanced Oil Recovery," in Handbook of Microemulsion Science and Technology, 1st. Ed.; Kumar P.; Mittal, K. L., Ed.; Marcel Dekker, Inc., New York,1999: 4743-4754.

Kellay, H.; Binks B. P.; Hendrikx, Y.; Lee, L. T.; Meunier, J., "Properties of Surfactant Monolayers in Relation to Microemulsion Phase Behaviour," Advances in Colloid and Interface Science, 1994, **49**, 85-112.

Kommuru, T. R.; Gurley, B.; Khan, M. A.; Reddy, I. K., "Self-emulsifying Drug Delivery Systems (SEDDS) of Coenzyme Q10: Formulation Development and Bioavailability Assessment," International Journal of Pharmaceutics 2001, **212** (2), 233-246.

Kunieda, H.; Fukui, Y.; Uchiyama, H.; Solans, C., "Spontaneous Formation of Highly Concentrated Water-in-Oil Emulsions (Gel-Emulsions)," Langmuir 1996, **12** (9), 2136-2140.

Kunieda, H.; Nakamura, K.; Davis, H. T.; Evans, D. F., "Formation of Vesicles and Microemulsions in a Water Tetraethylene Glycol Dodecyl Ether/Dodecane System," Langmuir 1991, **7** (9), 1915-1919.

Kunieda, H.; Shinoda, K., "Evaluation of the Hydrophile-Lipophile Balance (HLB) of Nonionic Surfactants," Journal of Colloid and Interface Science 1985, **107** (1), 107-121.

Lawrence, A. S. C., "Mechanism of Detergence," Nature 1959, **183**, 1491-1494.

Li, G-Z.; Mu, J-H.; Li, Y; Yuan; S-L., "An Experimental Study on Alkaline/Surfactant/Polymer Flooding Systems Using Nature Mixed Carboxylate," Colloids and Surfaces. A, Physicochemical and Engineering Aspects 2000, **173** (1-3), 219-229.

Lopez-Montilla, J. C.; Herrera-Morales, P. E.; Pandey, S.; Shah, D. O., "Spontaneous Emulsification: Mechanisms, Physicochemical Aspects, Modeling, and Applications," Journal of Dispersion Science and Technology 2002a, **23** (1-3): 219-268.

Lopez-Montilla, J. C.; Herrera-Morales, P. E.; Shah, D. O., "New Method to Quantitatively Determine the Spontaneity of the Emulsification Process," Langmuir 2002b **18** (11), 4258-4262.

Matalon, R., "Monolayer Penetration at the Oil-Water Interface. Part I. Effect of Salts on Emulsification," Transactions of Faraday Society 1950, **46**, 674-676.

McBain, J. W.; Woo, T-M., "Spontaneous Emulsification and Reactions Overshooting Equlibrium," Proceedings of the Royal Society 1937, **A 163**, 182-188.

Miller, C. A., "Spontaneous Emulsification Produced by Diffusion-A Review," Colloids and Surfaces 1988, **29**, 89-102.

Miller, C. A.; Hwan, R-N.; Benton, W. J.; Fort Jr., T., "Ultralow Interfacial Tensions and Their Relation to Phase Separation in Micellar Solutions," Journal of Colloid and Interface Science 1977, **61** (3), 554-568.

Minehan, W. T.; Messing, G. L., "Synthesis of Spherical Silica Particles by Spontaneous Emulsification," Colloids and Surfaces 1992, **63** (1-2), 181-187.

New, R. R. C.; Kirby, C. J., "Solubilisation of Hydrophilic Drugs in Oily Formulations," Advanced Drug Delivery Reviews 1997, **25** (1), 59-69.

Niesner, R.; Heintz, A., "Diffusion Coefficients of Aromatics in Aqueous," Journal of Chemical & Engineering Data 2000, **45** (6), 1121-1124.

Nishimi, T.; Miller, C. A., "Spontaneous Emulsification of Oil in Aerosol-OT/Water/Hydrocarbon Systems," Langmuir 2000, **16** (24), 9233-9241.

Nishimi, T.; Miller C.A., "Spontaneous Emulsification Produced by Chemical Reactions," Journal of Colloid and Interface Science 2001, **237** (2), 259-266.

Ozawa, K.; Solans, C.; Kunieda, H., "Spontaneous Formation of Highly Concentrated Oil-in-Water Emulsions," Journal of Colloid and Interface Science 1997, **188**, 275-281.

Pierce, R. C.; Trowbridge, J. R., "Phase-Behavior of Alcohol Ethoxylate-Oil-Water Systems and its Relationship to Detergency," Journal of the American Oil Chemists Society 1980, **57** (2), A118-A118.

Pillai, V; Kanicky, J. R.; Shah, D. O., "Application of Microemulsions in Enhanced Oil Recovery," in Handbook of Microemulsion Science and Technology, 1st. Ed.; Kumar, P. and Mittal, K. L., Eds.; Marcel Dekker, Inc., New York, 1999.

Pons, R.; Carrera, I.; Erra, P.; Kunieda, H.; Solans, C., "Novel Preparation Methods for Highly Concentrated Water in Oil Emulsions," Colloids and Surfaces A, Physicochemical and Engineering Aspects 1994, **91**, 259.

Pouton, C. W., "Formulation of Self-Emulsifying Drug Delivery Systems," Advanced Drug Delivery Reviews 1997, **25** (1), 47-58.

Pouton, C. W., "Lipid Formulations for Oral Administrations of Drugs: Non-Emulsifying, Self-emulsifying and "Self-microemulsifying" Drug Delivery Systems," European Journal of Pharmaceutical Sciences 2000, **11** (2) S93-S98.

Prince, L. M., "A Theory of Aqueous Emulsions .I. Negative Interfacial Tension at Oil/Water Interface," Journal of Colloid and interface Science 1967, **23** (2): 165-171.

Quincke, G., "Ueber Emulsionbildung und den Einfluss der Galle bei der Verdauung," Plüger Archiv für die Physiologie 1879, **19**, 129-144.

Quincke, G., "Ueber periodische Ausbreitung an Flüssigkeitsoberflächen und dadurch hervorgerufene Bewegungserscheinungen," Wiedemanss Annalen der Physik und Chemie. 1888, **35** (12), 580-642.

Raney, K. H.; Benton, W. J.; Miller, C. A., "Optimum Detergency Conditions with Nonionic Surfactans: I. Ternary Water-Surfactant-Hydrocarbon Systems," Journal of Colloid and Interface Science 1987, **117** (1), 282-290.

Rang, J. J.; Miller, C. A.; Hoffmann, H. H.; Thunig, C., "Behavior of Hydrocarbon/Alcohol Drops Injected into Dilute Solutions of an Amine Oxide Surfactant," Industrial & Engineering Chemistry Research 1996, **35** (9), 3233-3240.

Rang, M-J.; Miller, C.A., "Spontaneous Emulsification of Oils containing Hydrocarbon, Non-ionic Surfactant and Oleyl Alcohol," Journal of Colloid and Interface Science 1999, **209** (1), 179-192.

Raterman, K. T.; Shaeiwitz, J. A., "Liquid Solubilization Dynamics .2. Flux Enhancement by Interface Gel Formation," Journal of Colloid and Interface Science 1984, **98** (2), 394-405.

Rivas, H.; Gutierrez, X.; Zirrit, J. L.; Antón, R. E.; Salager, J. L., "Microemusion and Optimal Formulation Occurrence in pH-dependent Systems as Found in Alkaline-

Enhanced Oil Recovery," in Industrial Applications of Microemulsions, Solans, C.; Kunieda H. Eds., Marcel Dekker, Inc., New York. 1997.

Rosano, H. L.; Cavallo, J. L.; Lyons, G. B., "Mechanism of Formation of Six Microemulsion Systems," in Microemulsion Systems, 1st. Edition; Rosano, H., Clausse, M., Eds.; Surfactant Science Series; 24, 1987.

Rosen, M. J., "Detergency and its Modification by Surfactants," in Surfactants and Interfacial Phenomena. 2nd. Ed.; Wiley, New York, 1972.

Rudin, J.; Bernard, C.; Wasan, D. T., "Effect of Added Surfactant on Interfacial Tension and Spontaneous Emulsification in Alkali/Acidic Oil Systems," Industrial & Engineering Chemistry Research 1994, **33** (5), 1150-1158.

Ruschak, K. J.; Miller, C. A., "Spontaneous Emulsification in Ternary Systems with Mass Transfer," Industrial & Engineering Chemistry Fundamentals 1972, **11** (4), 534-540.

Salager, J. L., "Microemulsions," in Handbook of Detergents – part A: Properties, Broze, G. Ed.; Marcel Dekker Inc., New York, 1999.

Salager, J. L., "Phase Transformation and Emulsion Inversion on the Basis of Catastrophic Theory," in Encyclopedia of Emulsion Technology, 1st. Ed.; Becher, P. Ed.; Marcel Dekker, Inc., New York, 1983.

Saupe, A., "Textures, Deformations and Structural Order of Liquid Crystals," Journal of Colloid and Interface Science 1977, **58** (3), 549-558.

Schott, H., "Removal of Organic Soil from Fibrous Substrates," in Detergency: Theory and Test Methods, Part 1, Culter, W. G. Ed.; Dekker, New York, 1972.

Schulman, J. H.; Cockbain, E.G., "Molecular Interactions at Oil/Water Interfaces. Part I. Molecular Complex Formation and the Stability of Oil in Water Emulsions," Transactions of Faraday Society 1940, **36**, 651-661.

Shaeiwitz, J. A.; Chan, A. F-C.; Cussler, E. L.; Evans, D. F., "The Mechanism of Solubilization in Detergent Solutions," Journal of Colloid and Interface Science 1981 **84** (1), 47-56.

Shah, D. O., "Introduction," in Surface Phenomena in Enhanced Oil Recovery, Shah, D. O. Ed.; Plenum Press, New York. 1981.

Shah, D. O., "The Molecular Mechanism for Achieving Ultralow Interfacial Tension Minimum in a Petroleum Sulfonate/Oil/Brine System," Journal of Dispersion Science and Technology 1980, **1** (1), 55-95.

Shahidzadeh, N.; Bonn, D.; Aguerre-Chariol, O.; Meunier, J., "Spontaneous Emulsification: Relation to Microemulsion Phase Behavior," Colloids and Surfaces. A, Physicochemical and Engineering Aspects 1999, **147** (3), 375-380.

Shahidzadeh, N.; Bonn, D.; Meunier, J., "A New Mechanism of Spontaneous Emulsification: Relation to Surfactant Properties," Europhysics Letters 1997, **40** (4), 459-464.

Simion, F. A.; Starch, M. S.; Witt, P. S.; Woodford, J. D.; Edgett, K. J., "Hand and Body Lotions," in Textbook of Cosmetic Dermatology; 2nd Ed.; Baran, R.; Maibach, H. I. Eds.; Martin Dunitz 1998.

Sorensen, T. S., "Dynamics and Instability of Fluid Interfaces: Proceedings of a Meeting, Held at the Technical University of Denmark," in Lecture Notes in Physics, 1st. Ed.; Springer-Verlag, Lyngby, 1978; 105, 1-315.

Taber, J. J. "Research on Enhanced Oil Recovery. Past, Present and Future, "In Surface Phenomena in Enhanced Oil Recovery," Shah, D. O. Ed., Plenum Press, New York, 1981.

Theissen, O.; Gommper, G., "Lattice-Boltzmann Study of Spontaneous Emulsification," The European Physical Journal B 1999, **11** (1), 91-100.

Thompson, L., "The Role of Oil Detachment Mechanisms in Determining Optimum Detergency Conditions," Journal of Colloid and Interface Science 1994, **163** (1), 61-73.

Venter, D. L.; Nieuwoudt, I., "Liquid-liquid equilibria for phenolic compounds, neutral oils, and nitrogen bases at 313.15 K," Journal of Chemical & Engineering Data 2001, **46** (4), 813-822.
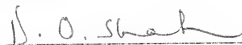
Wakerly, M. G.; Pouton, C. W.; Meakin, B. J.; Morton, F.S., "Self-Emulsification of Vegetable Oil-Nonionic Surfactant Mixture: a Proposed Mechanism of Action," American Chemical Society Symposium Series 1986, **311**, 242-255.

Walstra, P., "Emulsion Stability," in Encyclopedia of Emulsion Technology, 1st. Ed.; Becher, P.; Ed.; Marcel Dekker, Inc., New York, 1983.
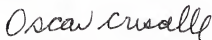
BIOGRAPHICAL SKETCH

Juan Carlos López Montilla was born on June 24, 1963, in Valle de La Pascua, Venezuela. He completed high school at the José Gil Fortour College in Valle de La Pascua and went to Simon Bolívar University (Sartanejas) to complete his bachelor's degree in chemical engineering in 1990. He joined the Chemical Engineering Department at the University of Los Andes and received his master's degree in chemical engineering from the group of Professor Jean Luis Salager in 1994 with a research on kinetics of solubilization of nonionic surfactants. After finishing his master's degree he joined the Chemical Engineering Department at the University of Los Andes. In 1998 he established contact with Dr. O. Crisalle, the professor in charge of recruiting new graduate students at the University of Florida. In January 1999 he started the Ph.D. program at the University of Florida. Dr. Crisalle asked him to talk with Dr. Dinesh Shah, who had conducted research on numerous interesting topics in surface chemistry. In February 2000, he joined Dr. Shah's group to work on spontaneous emulsification and completed the requirements for his Ph.D. degree in MAY 2002.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Dinesh O. Shah, Chair
Professor of Chemical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Oscar Crisalle
Associate Professor of Chemical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Chang Won Park
Professor of Chemical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Hassan El-Shall
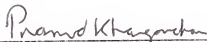Associate Professor of Materials Science and Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Brij Moudgil
Professor of Materials Science and
Engineering

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May 2003

Pramod P. Khargonekar,
Dean, College of Engineering

Winfred M. Phillips
Dean, Graduate School